European Commission

JRC TECHNICAL REPORTS

Report on the interlaboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in coconut oil

Stefanka Bratinova,
Lubomir Karasek

2017

Joint Research Centre

EUR 28741 EN

Contact information
Name: Stefanka Bratinova
EUROPEAN COMMISSION
Joint Research Centre
Address: Retieseweg 111, Geel 2440, Belgium
E-mail: Stefanka-Petkova.BRATINOVA@ec.europa.eu
Tel.: +32 (0)14 571 800

JRC Science Hub
https://ec.europa.eu/jrc

JRC 107710

EUR 28741 EN

PDF ISBN 978-92-79-72236-3 ISSN 1831-9424 doi:10.2760/816638

Luxembourg: Publications Office of the European Union, 2016

How to cite: Bratinova, S. and Karasek, L., *Report on the inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons: Four marker PAHs in coconut oil*, EUR 28741 EN, Publications Office of the European Union, Luxembourg, 2017, ISBN 978-92-79-72236-3, doi:10.2760/816638, JRC107710.

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Report on the interlaboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in coconut oil

Stefanka Bratinova,
Lubomir Karasek

268-PT Accredited by the
Belgian Accreditation Body (BELAC)

Table of content

Acknowledgements

The organisers would like to thank Piotr ROBOUCH from JRC-Geel F.5 for the thorough revision of this report as well as all participants for their cooperation.

Abstract

This report presents the results of the interlaboratory comparison (ILC) organised as a proficiency test (PT) by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EURL-PAHs) on the determination of the four EU marker PAHs, benz[a]anthracene (BAA), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF) and chrysene (CHR) in coconut oil.

The test material used in this exercise was commercial coconut oil, acquired from a local supermarket and spiked with a finely melted and homogenised mixture of PAHs in the EURL-PAH premises. In addition participants received a solution of PAHs in toluene or acetonitrile (solvent chosen by them) with known PAH content for the verification of their instrument calibration.

Twenty-eight officially nominated National Reference Laboratories (NRLs) and 23 Official food Control Laboratories (OCLs) of the EU Member States, Norway and Iceland participated to the study.

The test material was characterised by the EURL-PAH. The assigned values and their uncertainties were determined from independent replicate measurements on two different days by isotope dilution mass spectrometry which confirmed the nominal values derived from the gravimetric preparation.

Participants were free to choose their method of analysis. The performance of the participating laboratories in the determination of the target PAHs in the test material was expressed by both z-scores and zeta-scores. Additionally, the compliance of reported method performance characteristics was checked against specifications given in legislation.

This PT demonstrated the competence of the participating laboratories in the analysis of regulated PAHs in coconut oil. About 82% of the reported test results were assessed as satisfactory, based on the z-scores.

Participants were requested to assess the compliance of the sample against legislative limits. Eighty six percent of the participants assessed correctly the compliance of the test material.

1. Introduction

The European Commission's Joint Research Centre operates the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons in Food (EURL-PAH). One of its core tasks is to organise comparative testing for the National Reference Laboratories (NRLs) [1, 2].

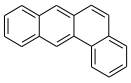
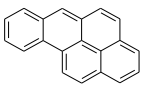
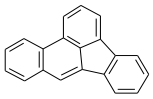
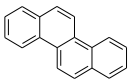
Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings. PAHs may be formed during the incomplete combustion of organic matter and can be found in the environment. In food, PAHs may be formed during industrial food processing and domestic food preparation, such as smoking, drying, roasting, baking, frying, or grilling [3, 4].

Of the many hundreds of different PAHs, benzo[a]pyrene is the most studied and often used as a marker for PAHs in ambient air and food [5]. The European Commission revised in 2011 legislation on PAHs taking thereby into consideration the conclusions drawn by the European Food Safety Authority (EFSA) on "Polycylic Aromatic Hydrocarbons in Food" [6]. New maximum levels (MLs) for the sum of four substances (PAH4) - benzo[*a*]pyrene (BAP), benz[*a*]anthracene (BAA), benzo[*b*]fluoranthene (BBF) and chrysene (CHR), (Table 1) were introduced whilst a separate maximum level for benzo[*a*]pyrene was maintained [7, 8].

Data have shown that coconut oil can contain higher amounts of PAH4 than other vegetable oils and fats. This is due to the proportionally higher presence of benz(a)anthracene and chrysene which cannot be easily removed during refinement of coconut oil. Specific maximum levels for coconut oil were therefore set at levels as low as reasonably achievable and taking into account the current technological possibilities of producing countries. As technological improvements in producing countries are expected, the levels of PAH in coconut oil should be regularly monitored with a view to assess the possibility for setting lower levels in the future.

In support to the implementation of the recommendation for constant monitoring of the levels of PAH in coconut oil laid down in Commission Regulation (EU) No 835/2011 of 19 August 2011, the EURL-PAH agreed with NRLs to focus in the 2017 EURL-PAH proficiency test (PT) exercise on the determination of PAHs in coconut oil.

Table 1: Names and structures of the four EU marker PAHs.

1	**Benz[*a*]anthracene (BAA)**		**2**	**Benzo[*a*]pyrene (BAP)**	
3	**Benzo[*b*]fluoranthene (BBF)**		**4**	**Chrysene (CHR)**	

2. Scope

As specified in Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with food and feed law, animal health and animal welfare rules [2], one of the core duties of EURLs is to organise comparative testing.

This PT aimed to evaluate the comparability of results reported by NRLs and EU official food control laboratories (OCLs) for the four EU marker PAHs in coconut oil. The appropriateness of the reported measurement uncertainty was also evaluated as this parameter is important in the compliance assessment of food with EU maximum levels.

The PT was designed and evaluated under the umbrella of the organiser's accreditation according to ISO/IEC 17043:2010 [10].

3. Setup of the exercise

3.1 Participating Laboratories

Only officially nominated NRLs and OCLs of the EU Member States were admitted as participants. The participants having registered to this exercise are listed in Tables 2 and Table 3.

Table 2: List of participating National Reference Laboratories (NRL)

Institute	*Country*
AGES GmbH	Austria
Scientific Institute of Public Health (WIV-ISP)	Belgium
Croatian Veterinary Institute - Branch Veterinary Institute of Split	Croatia
State General Laboratory	Cyprus
State Veterinary Institute Prague	Czech Republic
Bundesamt für Verbraucherschutz und Lebensmittelsicherheit	Germany
Danish Food Administration	Denmark
Danish Food and Veterinary Administration	Denmark
Health Board	Estonia
Centro Nacional de Alimentación. Agencia Española de Seguridad Alimentaria y Nutrición (AESAN)	Spain
Finnish Food Safety Authority Evira	Finland
LABERCA - Oniris	France
General Chemical State Laboratory	Greece
National Food Chain Safety Office, Feed Investigation	Hungary
Istituto Superiore di Sanità (ISS)	Italy
Public Analyst Laboratory	Ireland
Matis	Iceland
National Food and Veterinary Risk Assessment Institute	Lithuania

Laboratoire National de Santé	Luxembourg
Institute of Food Safety, Animal Health and Environment "BIOR"	Latvia
RIKILT	the Netherlands
NIFES	Norway
National Institute of Public Health - National Institute of Hygiene	Poland
ASAE - Autoridade de Seguranca Alimentar e Economica	Portugal
Swedish National Food Agency	Sweden
Institute of Public Health Maribor, Institute of Environmental Protection	Slovenia
State Veterinary and Food Institute Dolny Kubin	Slovakia
Fera Science Ltd	UK

From the 28 NRLs having registered, 2 NRLs did not report results.

Table 3: List of participating Official Food Control Laboratories (OCL)

Institute	*Country*
Institut für Umwelt und Lebensmittelsicherheit des Landes Vorarlberg	Austria
LVA GmbH	Austria
Laboratorium ECCA NV	Belgium
CVUA MEL	Germany
Institut für Hygiene und Umwelt	Germany
Landesuntersuchungsamt Rheinland-Pfalz	Germany
Eurofins WEJ Contaminants	Germany
Chemisches und Veterinäruntersuchungsamt Westfalen	Germany
LUFA-ITL GmbH	Germany
Berlin Brandenburg State Laboratory	Germany
INOVALYS	FRANCE
Laboratoire Departemental d'Analyses du Morbihan	FRANCE
Laboratoire de l'Environnement et de l'Alimentation de la Vendée	FRANCE
SCL	FRANCE
Laboratoire Phytocontrol	FRANCE
Arpal	Italy
Istituto Zooprofilattico Sperimentale del Lazio e della Toscana	Italy
Istituto Zooprofilattico Sperimentale dell'Umbria e delle Marche	Italy
Istituto Zooprofilattico Sperimentale	ITALY
Istituto Zooprofilattico Dell'Abruzzo e del Molise G.Caporale	Italy
ARPA LAZIO	ITALY
Dr. A. Verwey B.V.	The Netherlands
Nofalab B.V.	The Netherlands

All the (23) OCLs reported results.

3.2 Time frame

The PT was announced on the JRC public webpage (see ANNEX 1) and invitation letters were sent to the laboratories on December 2, 2016 (see ANNEX 2) with deadline for registration via EUSurvey webpage (see ANNEX 3) until January 6, 2017. Test samples were dispatched (see ANNEX 4) on January 23, 2017 and the deadline for reporting of results was set to February 20, 2017. The documents sent to the participants are presented in ANNEX 5.

3.3 Confidentiality

Confidentiality of the participants and their results towards third parties is guaranteed by non-disclosing the identity of participants to third parties, transmission of data through a dedicated web-based interface and a secure databank hosted by JRC. European commission rules on data protection were strictly followed as well.

3.4 Design of the proficiency test

The design of the PT foresaw triplicate analysis of the test items and reporting of individual results for individual analytes, based on the mass of the entire test portion (on product basis). Additionally "values for proficiency assessment", in the following denoted as "final values", were requested for both the single analytes and the sum of the four PAHs. They had to be expressed on product basis as well. All results had to be reported corrected for recovery; the "final values" had also to be accompanied by the respective expanded measurement uncertainties and the corresponding coverage factors. Only final values were used for performance assessment.

Furthermore, participants were requested to report details of the performance of the applied analytical method (see ANNEX 9) and to assess the compliance of the sample according to the current legislative limits.

Each participant received at least one ampoule of a solution of the target PAHs (2 ml), with known content, and one amber glass vial containing the coconut oil test material.

4. Test materials

4.1 Preparation

The test item of this PT was coconut oil. Participants also received a solution of the 4 EU markers PAHs either in acetonitrile or in toluene (according to their choice, see ANNEX 3) with known concentrations, which allowed them to check their instrument calibration against an independent reference. Participants received the technical specifications (see ANNEX 6) of the chosen solution together with the test material.

The coconut oil test item was prepared at the EURL-PAH starting from 2 kg of coconut oil, acquired at a local supermarket. The material was melted, spiked with a mixed solution of NIST certified material in toluene (NIST SRM 2260a) and a BCR solution of chrysene (BCR269) and homogenized for 24 hours. Aliquots of about 5 g were packed in amber glass screw cap vials and stored in a refrigerator at about 4 °C.

The standard solutions were prepared from neat reference substances checked against the certified reference materials (NIST). Single standard stock solutions of each analyte were produced from neat substances on a microbalance and dissolution in toluene. Mixed standards were prepared gravimetrically from the single standard stock solutions in the respective solvents and further diluted to the concentrations specified in ANNEX 6. The standard solutions were ampouled under inert atmosphere and flame sealed in 2 ml amber glass ampoules.

4.2 Homogeneity and stability

The coconut oil was tested for significant inhomogeneity, according to the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, and for sufficient homogeneity according to ISO 13528:2015 [11]. Homogeneity experiments consisted of sample extraction by pressurized liquid extraction, size-exclusion chromatography followed by solid phase extraction clean-up and gas chromatography with mass spectrometric detection. The method precision complied with the requirements laid down in ISO 13528:2015 [11].

Homogeneity experiments included duplicate analysis of 10 samples randomly selected along the filling sequence among the amber glass vials prepared for dispatch. The duplicate analyses were performed in random order. The test material was rated sufficiently homogenous at a sample intake of 0.1 g and no trend was observed. Details of the homogeneity tests are given in ANNEX 7.

The stability of the test material was evaluated following the requirements in ISO 13528:2015. Six randomly selected samples were stored at three different conditions for 9 weeks, covering the period from the dispatch of the material to the end of the submission of the results.

The first set of 3 samples was stored at room temperature as recommended conditions (~ 21 °C). The second set of 3 samples was stored for the whole period of the study in a deep freezer at the reference temperature (~ -80 °C) and the third set was stored at elevated temperature at 40 °C for one week, mimicking the possible temperature increase during the transportation. After the deadline for reporting of results had expired, all 9 samples were analysed in duplicate under repeatability conditions.

No significant differences of the analyte contents of the test samples were found. Hence stability of the test samples can be assumed over the whole period of the study provided that the recommended storage conditions were applied (ANNEX 8).

4.3 Assigned value, corresponding uncertainty, and standard deviation for proficiency assessment

The assigned values were determined at the EURL-PAH applying isotope dilution mass spectrometry, a method implemented and validated at the EURL-PAH. This implied the preparation of standard solutions from two totally independent sources - NIST SRM 2260a and neat certified reference materials BCR® from the JRC. The analytical method was fully validated by collaborative trial and is accredited according to ISO 17025. This method became recently a European standard EN16619:2015 [12].

The associated uncertainties (u_{Xpt}) of the assigned values were calculated combining the uncertainty of the characterization (u_{char}) with the contributions for homogeneity (u_{bb}) and stability (u_{st}) in compliance with ISO/IEC Guide 98 (GUM) [13]:

$$u_{Xpt} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{st}^2} \qquad \text{Eq. 1}$$

The stability study confirmed that the material was stable and the uncertainty contribution due to stability was set to zero ($u_{st} = 0$) for all analytes. The contribution from homogeneity (u_{bb}) to the standard uncertainty of the assigned value ($u(x_{pt})$) was calculated using SoftCRM [16].

It should be noted that the assigned values, determined by the EURL-PAHs, were in full agreement with the gravimetrically calculated values from the spiking experiment.

The assigned value for the sum of 4 PAH was calculated from the individual assigned values, and its corresponding uncertainty was calculated from the uncertainties of the individual assigned values according to the law of error propagation.

The standard deviation for proficiency assessment, σ_{pt}, was set for the individual analytes equal to the maximum tolerable uncertainty (u_f), calculated applying Equation 2 [8]. A limit of

detection (LOD) value of 0.30 µg/kg, and the numerical factor α equal to 0.2 as prescribed in Regulation (EC) 836/2011 [8], for the concentration level (C) of interest were used.

$$u_f = \sqrt{(\mathrm{LOD}/2)^2 + (\alpha \mathrm{C})^2} \qquad \text{(Equation 2)}$$

The uncertainty for the SUM4PAH parameter (later set as σ_{pt} for the SUM4PAH) was calculated applying the law of error propagation of the maximum tolerable uncertainties of the individual PAHs.

Table 4: Assigned values (X_{pt}), associated expanded uncertainties ($U(x_{pt})$, k=2) and standard deviation for proficiency assessment ($\sigma_{pt)}$ (for the coconut oil test item, expressed based on mass of entire product (on product basis).

Analyte	Analyte short name	x_{pt}	$U(x_{pt})$	σ_{pt} (= u_f)		$u(x_{pt})/\sigma_{pt}$
		µg/kg	µg/kg	µg/kg	%	
Benz[*a*]anthracene	BAA	2.07	0.09	0.44	21.3	0.10
Chysene	CHR	10.07	0.80	2.02	20.1	0.20
Benzo[*b*]fluoranthen	BBF	3.56	0.29	0.73	20.4	0.18
Benzo[*a*]pyrene	BAP	2.18	0.14	0.46	21.2	0.15
Sum of the four PAHs	SUM4PAH	17.87	0.87	2.20	12.5	

As for all analytes, the uncertainty of the assigned values is lower than 0.3 time's standard deviation of the PT

$u(x_{pt}) < 0.3*\sigma_{pt,}$

it can be considered as negligible and does not need to be included in the interpretation of the results of the PT.

5. Evaluation of laboratories

5.1 General

The performance of the laboratories in the determination of the target PAHs in the test material was assessed using z-scores [11]. Zeta-scores were calculated in addition taking into account the measurement uncertainties reported by the participants.

The results as reported by participants are listed in ANNEX 10.

The compliance with legislation of the performance characteristics of the analytical methods applied by the participants for the analysis of the test sample was evaluated as well.

5.2 Evaluation parameter

z-scores

z-scores were calculated based on the final values (x_i) as follows:

$$z = \frac{\left(x_i - x_{pt}\right)}{\sigma_{pt}} \qquad \text{(Equation 3)}$$

where X_{pt} is the assigned value, and σ_{pt} the standard deviation for proficiency assessment.

zeta-scores

In contrast to z-scores, zeta-scores describe the agreement of the reported ranges ($x_i \pm u(x_i)$) with the respective assigned ranges ($x_{pt} \pm u(x_{pt})$). The following equation applies:

$$zeta = \frac{x_i - x_{pt}}{\sqrt{u(x_i)^2 + u(x_{pt})^2}} \qquad \text{(Equation 4)}$$

Whenever participants did not report measurement uncertainties, $u(x_i)$ was set to zero, which increases the zeta-score.

Performance classification scheme

The performance of the laboratories was classified according to ISO/IEC 17043:2010 [10]. The following scheme is applied for the interpretation of both z-scores and zeta scores:

	|score| ≤ 2.0	= satisfactory performance
2.0 <	|score| < 3.0	= questionable performance
	|score| ≥ 3.0	= unsatisfactory performance

5.3 Evaluation of results

z-scores were attributed only to the "final values". The individual results of replicate analyses were not rated.

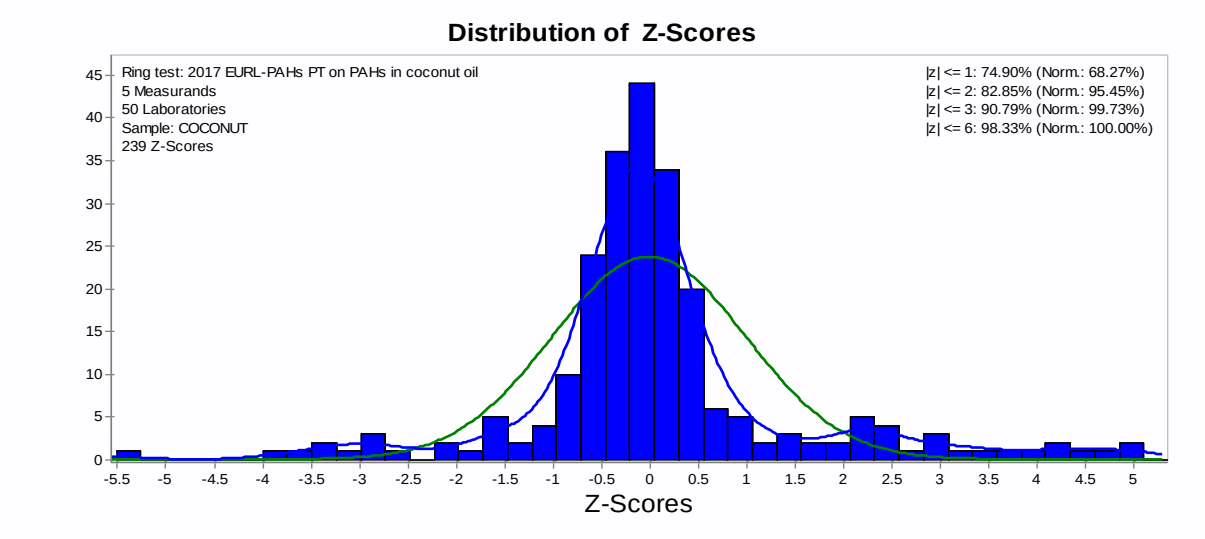
Each laboratory had to report a total of 5 results; therefore the expected total number of results of the 51 participants was 255. Two NRLs did not report results. The results as reported by participants are presented in ANNEX 11.

Statistical evaluation of the results was performed using PROLab software [13]. While the isotope dilution mass spectrometry results provided by the EURL-PAH were set as assigned values, Algorithm A+S of ISO 13528:2015 [11] was applied to compute the robust means and robust standard deviations (as additional information).

The confidence intervals of the robust means calculated from the participants' results (ANNEX 11, Kernel density plot) are in good agreement with the confidence intervals of the assigned values. The robust standard deviation of the results of participants reported for all analytes in the coconut oil test material were lower than the maximum tolerable uncertainties (u_f) calculated using Equation 2.

Figure 1 shows that 83 % and 74 % of the participants obtained satisfactory z- and zeta-scores, respectively, (|z or zeta| ≤ 2). Only 11 % of the results fall into the unsatisfactory performance range (|z or zeta| > 3).

Figure 1: Histogram of z- and zeta-scores for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH



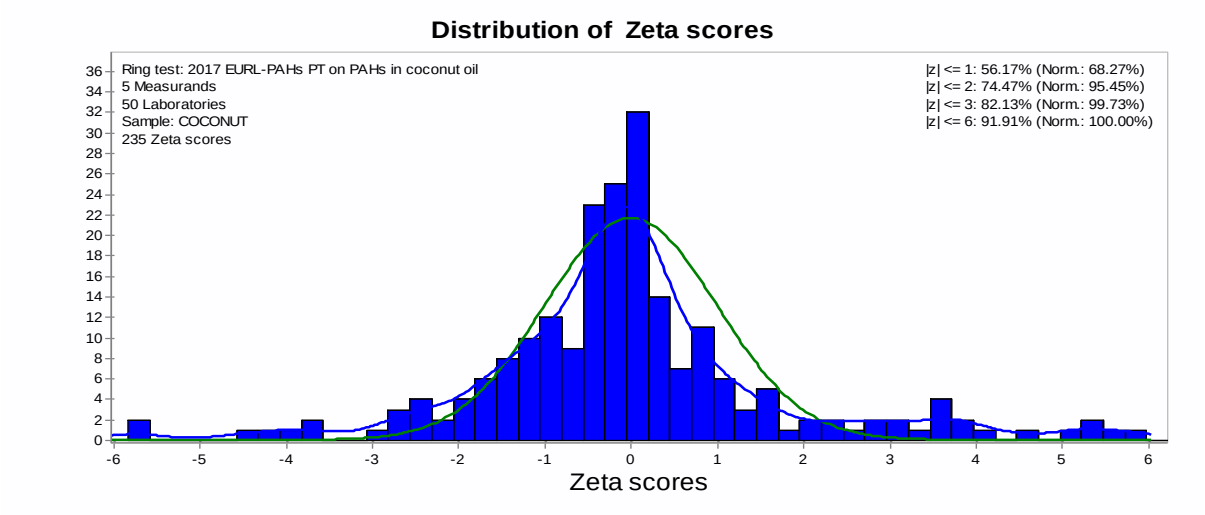


Figure 2: Percentage/number (label on bars) of laboratories with satisfactory (green), questionable (yellow) and unsatisfactory performance (red)

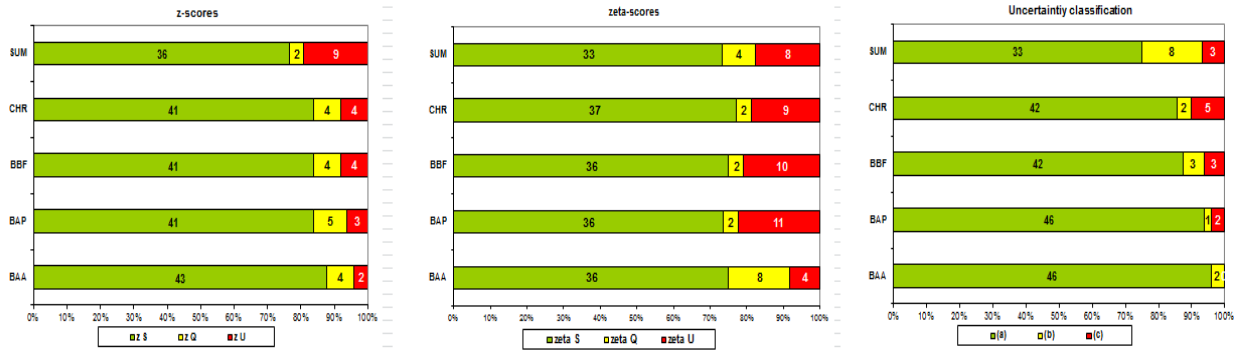


Figure 2 presents the distribution of performance ratings (z- and zeta-scores) for the individual measurands, together with the evaluation of reported uncertainties. The criteria for uncertainty evaluation are explained hereafter. Annex 11 presents the reported results and the corresponding evaluation.

Figures 3a and 3b provide overviews of the individual z-scores and zeta-scores assigned to the results reported for the coconut oil test material by NRLs and OCLs, respectively. The larger the triangles, the larger the differences to the assigned values. Green, yellow and red triangles represent "satisfactory", "questionable" and "unsatisfactory" performances, respectively. Only |z or zeta|> 3 scores are indicated next to the triangles.

The numerical values of the calculated z (zeta)-scores are presented in the tables of Annex 11. The "Questionable" and "Unsatisfactory" scores are highlighted in yellow and red backgrounds, respectively.

The distributions of results for the individual analytes are displayed in the figures of ANNEX 11 together with respective Kernel density plots. The figures show for each analyte individual analysis results of the three replicate determinations.

Thirty-one participants obtained satisfactory z-scores for all five measurands. Six additional laboratories reported satisfactory results for 4 measurands (out of 5). The remaining five participants were less successful, as they reported at maximum two satisfactory results. Four NRLs had no satisfactory z-scores, while two other NRLs did not report any results. It should be noted that the coconut oil test material was spiked with the NIST standard mixture containing 36 PAHs, which may have introduced interferences from non-target PAHs.

The plausibility of the uncertainty statements of the laboratories was assessed in the current PT classifying every reported uncertainty into three groups (Annex 11 and Figure 2) according to the following rules:

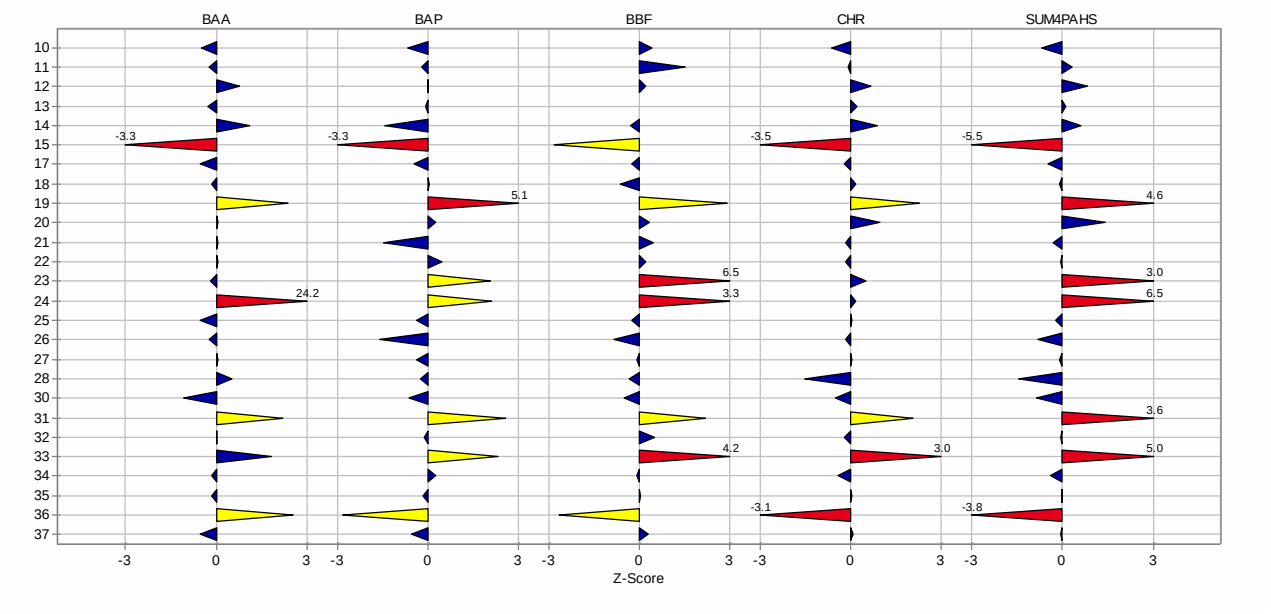
The standard measurement uncertainty from a laboratory ($u(x_i)$) is most likely to fall in a range between a minimum and a maximum uncertainty (case "a": $u_{min} \leq u(x_i) \leq u_{max}$). The minimum uncertainty (u_{min}) is set for the respective analyte to the standard uncertainty of the assigned value ($u(x_{pt})$). This is based on the assumption that it is unlikely that a laboratory carrying out the analysis on a routine basis would determine the measurand with a smaller measurement uncertainty than that achieved in the experiments for the characterisation of the test material, which were based on isotope dilution mass spectrometry applying bracketing calibration. The maximum uncertainty is set to the standard deviation accepted for the assessment of results (σ_{pt}), in this PT set to the maximum threshold given by the "fitness-for-purpose" function U_f. Consequently, case "a" becomes: $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$.

If $u(x_i)$ is smaller than $u(x_{pt})$ (case "b": $u(x_i) < u(x_{pt})$) the laboratory might have underestimated its measurement uncertainty.

If $u(x_i)$ is larger than σ_{pt} (case "c": $u(x_i) > \sigma_{pt}$) the laboratory might have overestimated its measurement uncertainty, or applied an analytical method that was not fit-for-purpose. Both cases require corrective action!

Although the estimation of measurement uncertainties improved over recent PT rounds, still the rate of the satisfactory zeta scores is much lower than the one for z-scores. The EURL-PAH should continue to pay attention to this parameter in the PTs to come, as measurement uncertainty has major implications on the assessment of compliance of food according to European legislation as will be seen later on in this report.

Figure 3a: Graphical presentation of z- and zeta- scores corresponding to the "final values for proficiency assessment" reported by the NRLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter in the coconut oil test material.



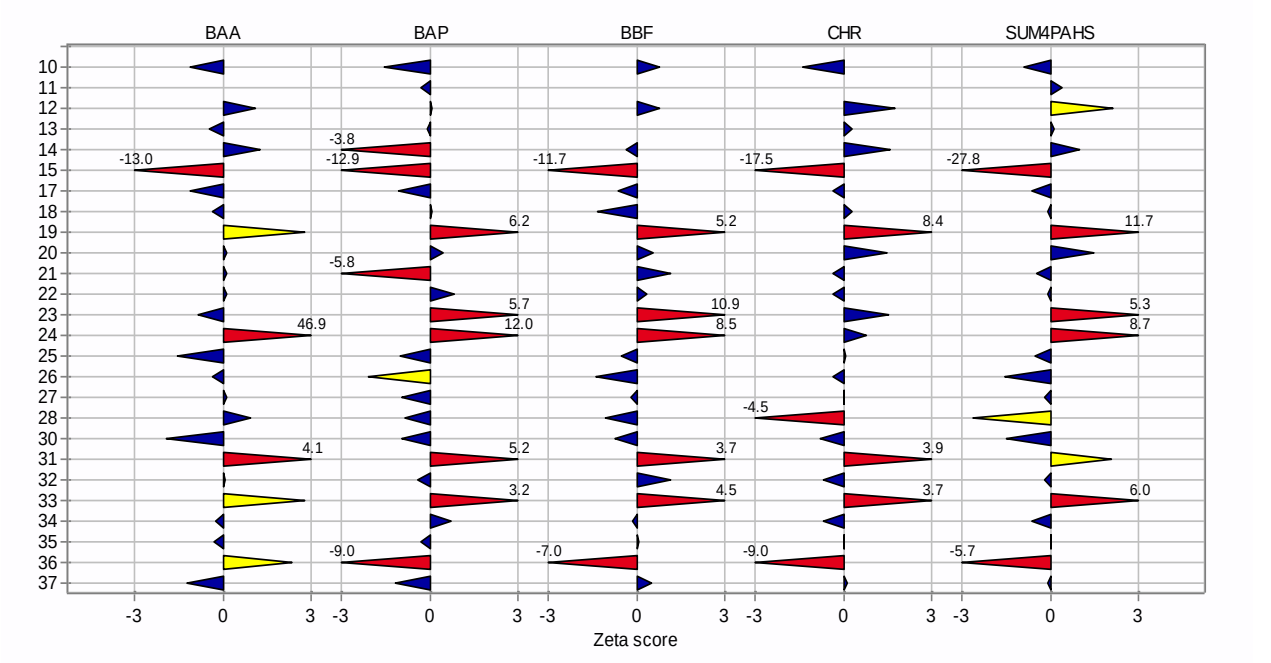
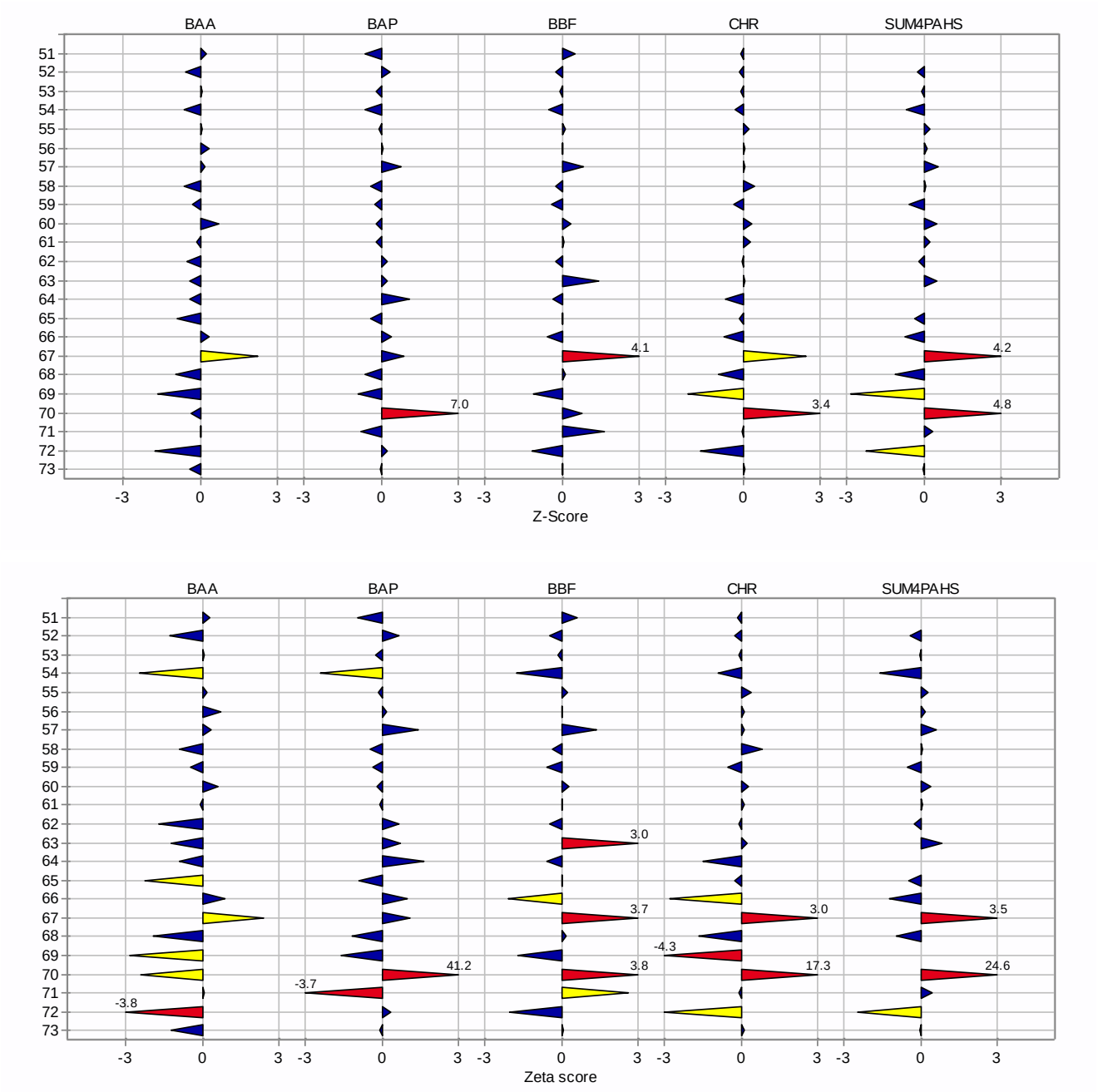


Figure 3b: Graphical presentation of z and zeta-scores corresponding to the "final values for proficiency assessment" reported by the OCLs for the contents of BAA, BAP, BBF, CHR, and the SUM4PAH parameter in the coconut oil test material.



As indicated by the Kernel density plots (Annex 11) the distributions of results are close to a Gaussian distribution. The major modes are close to the assigned (reference) values and to the robust means calculated from the reported results. This confirms that the measurement of PAHs in coconut oil is under statistical control. No influence from the analytical techniques used (GC-MS; GC-MS/MS or HPLC) could be identified.

Inconsistencies were observed in the number of significant digits reported for the measurement results and associated uncertainties. The EURL-PAH will address this issue again at the next workshop, as a harmonised reporting of results is necessary for proper implementation of the EU legislation.

Unlike previous PT exercises organised by the EURL-PAH, OCLs performed better than NRLs in the present PT (see Figures 3a and 3b). This may be attributed to the complex mixture of PAHs contained in the investigated matrix. The NRLs having reported questionable or unsatisfactory results are urged to investigate and improve the selectivity of their analytical method, in order to avoid any potential cross interferences.

5.4 Compliance assessment

The correct interpretation of results is as important as reporting accurate measurement results. The maximum levels (ML) for BAP and for the SUM4PAH are set in Commission Regulation (EU) No 2015/1933, as 2.0 µg/kg and 20.0 µg/kg, respectively. The assigned value for the SUM4PAH in the test item (17.9 ± 0.9 µg/kg) is below the corresponding ML. This is not the case for BAP in the coconut oil, but the lower level of the assigned expanded range (2.18 ± 0.14 µg/kg) almost coincides with the specific ML*. Hence, the coconut oil test item used in this PT is considered as "compliant".

The EURL requested participants to assess the compliance of the test item, taking into account their analysis results and the current legislative limits. Figure 4 presents all reported results with their associated expanded uncertainties for BaP and SUM4PAH, together with the corresponding ML defined in legislation (see red lines).

The decision criterion for non-compliance is specified in Commission Regulation (EC) No 333/2007 [7]. "*A lot or sub-lot shall be rejected if the content value of this lot or sub-lot is beyond reasonable doubt above the respective maximum level given in legislation, taking into account the expanded measurement uncertainty and correction for recovery*". This translates in a content value that is derived from the measured and recovery corrected content value by subtraction of the expanded uncertainty (k=2). Such situations occur (see Figure 4) when the lower end of the error bar (representing the expanded measurement uncertainty) associated with the reported result (black dot) is above the red line.

Thirty two laboratories (out of 49) correctly assessed the test sample as compliant (Figure 7), while 10 laboratories wrongly classified the sample as non-compliant, based on their biased (overestimated) results. Five laboratories (13, 27, 53, 62 and 67) provided an assessment statement with no proper justification, while the last two participants (63 and 69) did not reply to the questionnaire. As a consequence, additional attention should be paid in future to the interpretation of the analytical results.

* After rounding up to the first decimal after comma, e.g. (2.18-0.14 = 2.04 ≈ 2.0 = ML, all values in µg/kg)

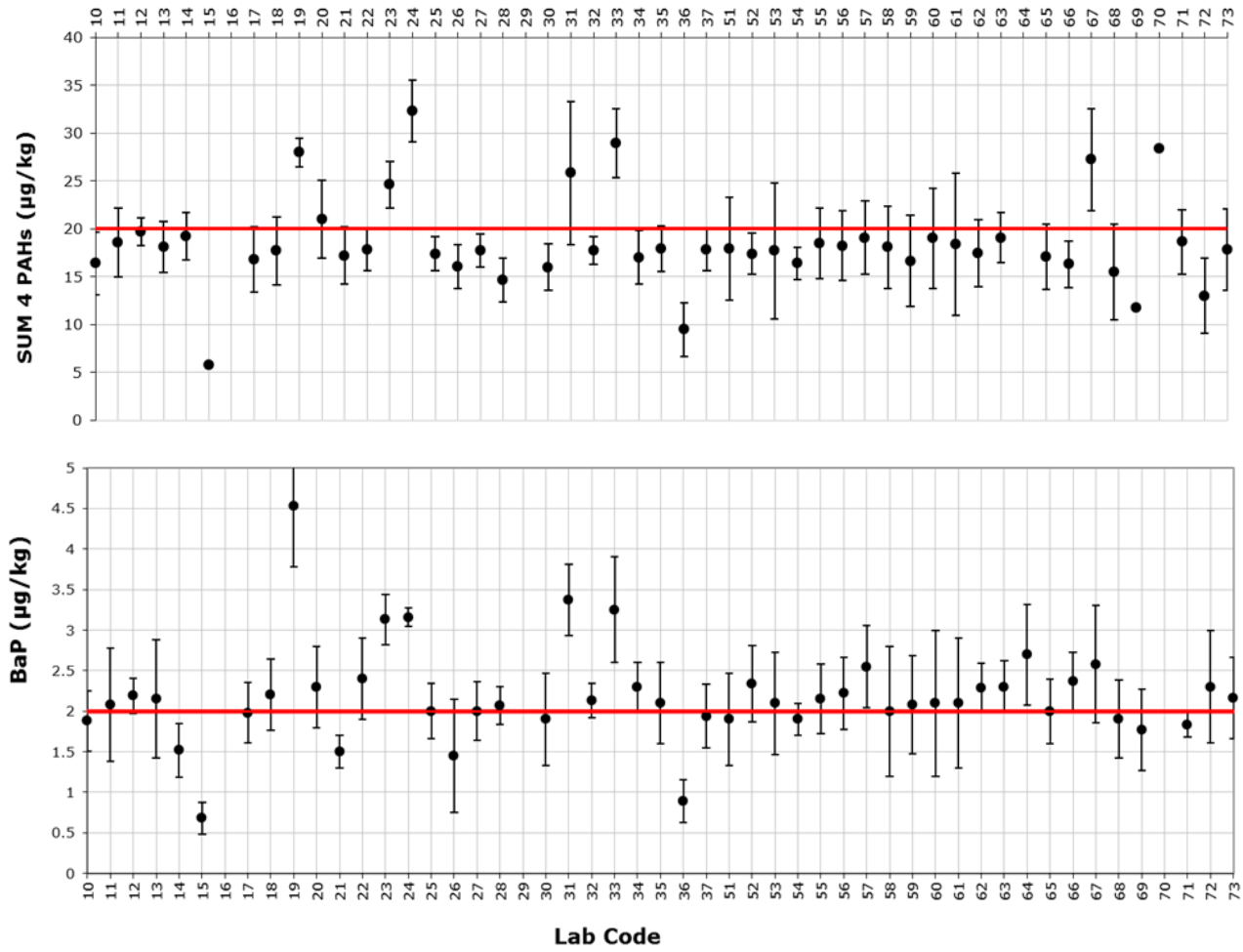


Figure 4. Distribution of the results reported by the participants and the associated expanded measurement uncertainties for BaP and the SUM PAHs in relation to the MLs. The solid red lines represent the current maximum levels (MLs)

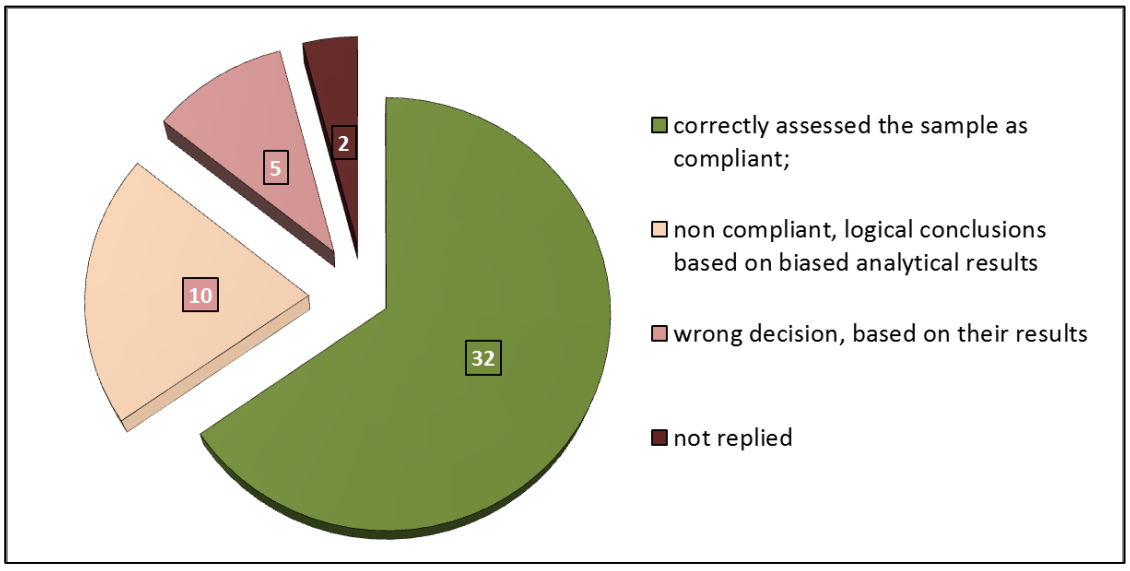


Figure 5. Compliant assessment statements issued by the participants in relation with the Commission Regulation (EU) No 2015/1933 for the coconut oil sample.

5.5 Additional information extracted from the questionnaire

Additional information was gathered from the questionnaire filled by the participants (ANNEX 9). Data are presented as reported.

99% of the participants had previous experience with the determination of PAHs in fat/oil as this food category has been regulated for many years. All of them used validated methods with the majority referring to in-house/laboratory methods.

Concerning the applied instrumental techniques a slight trend towards replacing the GC/MS analysis with GC/MS-MS could be noticed when comparing with the previous years (Fig.6).

Seven participants prepared their calibration solutions in the laboratory from neat compounds, 27 used commercial standard mixtures in solvent and 12 used both approaches for cross checking (Fig.7). No significant difference was noticed between the results of these tree populations.

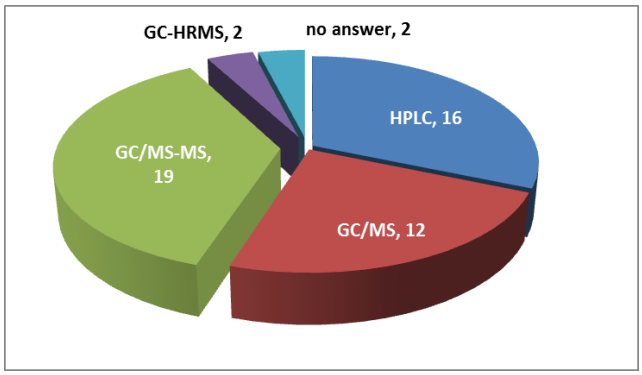


Figure 6: Distribution amongst the techniques applied for analysis of PAHs in coconut oil (number of participants using the responding technique).

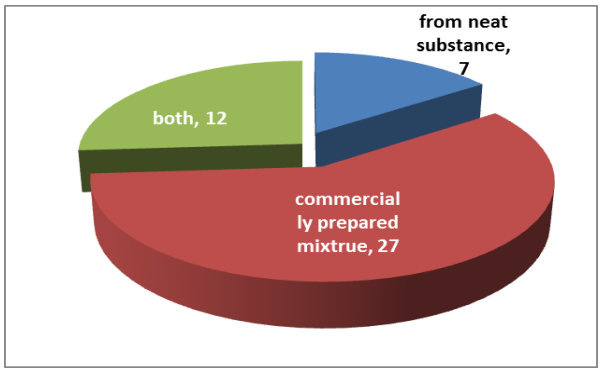


Figure 7: Type of calibrants used for analysis of PAHs in coconut oil (number of participants using the responding calibrants.

6. Follow-up actions for underperforming laboratories

All laboratories having "questionable" or "non-satisfactory" performance ratings (z-scores) are urged to perform a root cause analysis, and to implement the required corrective actions.

The EURL will set up follow-up measures in due time for all NRLs that received |z-scores| > 3 for at least one of the four PAHs (BAA, BAP, BBF, and CHR), as required by Regulation (EC) 882/2004, and by the "Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with European Union Reference Laboratories (EURLs) activities". As an immediate action, these laboratories shall perform a root-cause-analysis, and shall report to the EURL-PAH in writing (i) the identified cause for their underperformance, as well as (ii) the corrective actions that they will implement. A repetition of this PT is envisaged in the near future.

Conclusion

Forty nine participants reported analysis results. The performance of most participants was satisfactory. More than 82 % of the results reported by NRLs and OCLs, respectively, obtained satisfactory performance ratings. The lower rate of successful performance compared to previous PTs on oil might be attributed to the complexity of the spiked solution, containing more than the four indicator PAHs and the possible interferences due to that fact.

The large majority of participants in this interlaboratory comparison applied analytical methods which, with regard to performance characteristics, were compliant with EU legislation.

Overall, NRLs reported good measurement uncertainty estimates, thus demonstrating the effectiveness of the various PTs and workshop presentations, organised by the EURL-PAHs in the past 10 years.

As for compliance assessment, the majority of the participants (65 %) stated correctly (providing proper justification) that the test item was compliant with the maximum levels set by Commission Regulation (EU) No 2015/1933 for BAP and the SUM4PAHs in coconut oil. 20% of the laboratories reported biased (overestimated) results and concluded that the test item is non-compliant. The remaining laboratories wrongly interpreted their analytical results. This clearly indicates that compliance assessment remains to be improved.

References

1 EU, Regulation (EC) No 776/2006 the European Parliament and of the Council of 23 May 2006 amending Annex VII to Regulation (EC) No 882/2004 of the European Parliament and of the Council as regards Community reference laboratories. Official Journal of the European Union, 2006. **L 136**: p. 3-8.

2 EU, Regulation (EC) No 882/2004 of the European Parliament and of the Council of 29 April 2004 on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Official Journal of the European Communities, 2004. **L191**: p. 1-52.

3 EU, Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food. SCF/CS/CNTM/PAH/29 Final, 4 December 2002

4 IARC Monographs on the Evaluation of Carcinogenic Risks to humans (2006). Available from: http://monographs. iarc.fr/ENG/Classification/ crthgr01.php

5 EU, Commission Recommendation (2005/108/EC) of 4 February 2005 on the further investigation into the levels of polycyclic aromatic hydrocarbons in certain foods. Official Journal of the European Union, 2005. L 34: p. 43-45.

6 EFSA, Polycyclic Aromatic Hydrocarbons in Food, Scientific Opinion of the Panel on Contaminants in the Food Chain, (Question N° EFSA-Q-2007-136), Adopted on 9 June 2008,

7 EU, Commission Regulation (EC) No 835/2011 of 19 August 2011, amending Regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in foodstuffs setting maximum levels for certain contaminants in foodstuffs. Official Journal of the European Union, 2006. **L 215:** p. 4-8.

8 EU, Regulation (EU) No 836/2011 the European Parliament and of the Council of 19 August 2011 amending Regulation (EC) No 333/2007, laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs: Official Journal of the European Union, 2011. **L 215**: p. 9-16 .

9 Commission Regulation (EU) 2015/1933 of 27 October 2015 amending Regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in cocoa fibre, banana chips, food supplements, dried herbs and dried spices

10 ISO/IEC 17043:2010 "Conformity assessment - General requirements for proficiency testing providers". International Organization for Standardization, Geneva, Switzerland

11 ISO 13528:2015 "Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons". International Organisation for Standardization, Geneva, Switzerland

12 EN 16619:2015 Food analysis - Determination of benzopyrene, benzanthracene, chrysene and benzofluoranthene in foodstuffs by gas chromatography mass spectrometry (GC-MS)

13 PROLab, Software for PT programs and collaborative studies; http://quodata.de/en/software/for-interlaboratory-tests.html

14 IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories. M. Thomson et al., Pure Appl. Chem., Vol. 78, No. 1, pp. 145–196, 2006

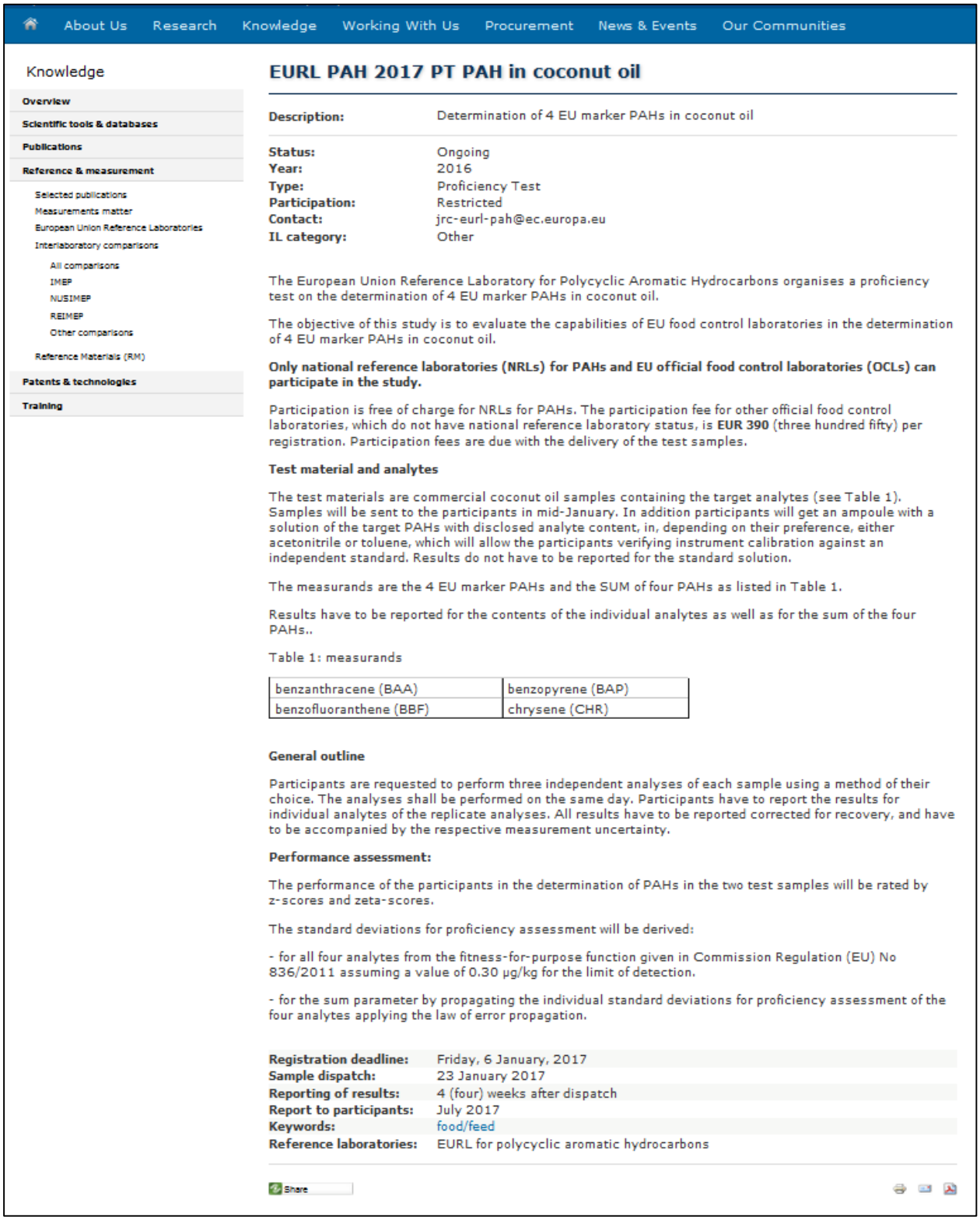
15 ISO/IEC Guide 98-3:2008 "Evaluation of measurement data – Guide to the expression of uncertainty in measurement" International Organization for Standardization, Geneva, Switzerland

16 SoftCRM, (n.d.). http://www.eie.gr/iopc/softcrm/index.html.

List of abbreviations and definitions

BAA	Benz[*a*]anthracene
BAP	Benzo[*a*]pyrene
BBF	Benzo[*b*]fluoranthene
CHR	Chrysene
EC	European Commission
EFSA	European Food Safety Authority
EU	European Union
EURL-PAH	European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons
ILC	Interlaboratory comparison
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
LOD	Limit of Detection
LOQ	Limit of Quantitation
ML	Maximum level
NIST	National Institute of Standards and Technology
NRL	National Reference Laboratory
OCL	Official food control laboratory
PAHs	Polycyclic aromatic hydrocarbons
PT	Proficiency test
SUM4PAH	Sum of the four markers PAHs

ANNEX 1: Announcement of the PT on the JRC webpage



About Us | Research | Knowledge | Working With Us | Procurement | News & Events | Our Communities

Knowledge

- Overview
- Scientific tools & databases
- Publications
- Reference & measurement
  - Selected publications
  - Measurements matter
  - European Union Reference Laboratories
  - Interlaboratory comparisons
    - All comparisons
    - IMEP
    - NUSIMEP
    - REIMEP
    - Other comparisons
  - Reference Materials (RM)
- Patents & technologies
- Training

EURL PAH 2017 PT PAH in coconut oil

Description: Determination of 4 EU marker PAHs in coconut oil

Status: Ongoing
Year: 2016
Type: Proficiency Test
Participation: Restricted
Contact: jrc-eurl-pah@ec.europa.eu
IL category: Other

The European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons organises a proficiency test on the determination of 4 EU marker PAHs in coconut oil.

The objective of this study is to evaluate the capabilities of EU food control laboratories in the determination of 4 EU marker PAHs in coconut oil.

Only national reference laboratories (NRLs) for PAHs and EU official food control laboratories (OCLs) can participate in the study.

Participation is free of charge for NRLs for PAHs. The participation fee for other official food control laboratories, which do not have national reference laboratory status, is **EUR 390** (three hundred fifty) per registration. Participation fees are due with the delivery of the test samples.

Test material and analytes

The test materials are commercial coconut oil samples containing the target analytes (see Table 1). Samples will be sent to the participants in mid-January. In addition participants will get an ampoule with a solution of the target PAHs with disclosed analyte content, in, depending on their preference, either acetonitrile or toluene, which will allow the participants verifying instrument calibration against an independent standard. Results do not have to be reported for the standard solution.

The measurands are the 4 EU marker PAHs and the SUM of four PAHs as listed in Table 1.

Results have to be reported for the contents of the individual analytes as well as for the sum of the four PAHs..

Table 1: measurands

benzanthracene (BAA)	benzopyrene (BAP)
benzofluoranthene (BBF)	chrysene (CHR)

General outline

Participants are requested to perform three independent analyses of each sample using a method of their choice. The analyses shall be performed on the same day. Participants have to report the results for individual analytes of the replicate analyses. All results have to be reported corrected for recovery, and have to be accompanied by the respective measurement uncertainty.

Performance assessment:

The performance of the participants in the determination of PAHs in the two test samples will be rated by z-scores and zeta-scores.

The standard deviations for proficiency assessment will be derived:

- for all four analytes from the fitness-for-purpose function given in Commission Regulation (EU) No 836/2011 assuming a value of 0.30 µg/kg for the limit of detection.

- for the sum parameter by propagating the individual standard deviations for proficiency assessment of the four analytes applying the law of error propagation.

Registration deadline: Friday, 6 January, 2017
Sample dispatch: 23 January 2017
Reporting of results: 4 (four) weeks after dispatch
Report to participants: July 2017
Keywords: food/feed
Reference laboratories: EURL for polycyclic aromatic hydrocarbons

Share

ANNEX 2: Announcement of the PT via e-mail

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate F – Health, Consumers and Reference Materials

Ref. Ares(2016)6755859 - 02/12/2016

Geel, 01/12/2016
Ref. Ares(2016) 6755859 - 02/12/2016

Inter-laboratory comparison on the determination of four EU marker PAHs in coconut oil

Dear Madam/Sir,

Registration for participation in the inter-laboratory comparison study organised by the EURL PAH on the determination of the 4 marker PAHs in cocoa oil is **open until 6th January 2017**.

Participation is mandatory and free of charge for National Reference Laboratories (NRLs) for PAHs. Confidentiality of data is granted.

In support to the NRLs, and to facilitate fulfilling their tasks as defined in Regulation (EC) No 882/2004, EU Official Food Control Laboratories (OCLs) falling under the responsibility of the NRLs may participate in the study. **The participation fee for official food control laboratories is 390 Euro per participation.**

The target analytes are listed in the following Table.

benz[*a*]anthracene (BaA)
benzo[*b*]fluoranthene (BbF)
benzo[*a*]pyrene (BaP)
chrysene (CHR)
SUM of the 4 marker PAHs

Results have to be reported corrected for recovery and accompanied by the respective measurement uncertainty for both the individual PAHs and the sum of the four marker PAHs. **Additionally participants will be asked to perform compliance assessment according to the corresponding legislative limits**

Each participant will be provided with an amber glass vial containing approximately 5 g of coconut oil test sample

Participants will also receive a standard solution in either acetonitrile or toluene with disclosed content; which may be used for verification of instrument calibration.

This inter-laboratory comparison is organised under accreditation to ISO 17043.

Detailed information will soon be available on the EURL website:
http://irmm.jrc.ec.europa.eu/EURLs/EURL_PAHs/interlaboratory_comparisons/Pages/index.aspx

Timing:

- **Deadline for registration: 6th January 2017**
- Dispatch of samples: **second half of January**. A detailed outline of the study will be included in the parcels. Participants will be asked to return a sample receipt to the organiser
- Deadline for reporting of results: **4 weeks after the dispatch of the samples**.

Registration procedure:

You are invited to register via following link:

https://ec.europa.eu/eusurvey/runner/2017_EURL_PAH_PT_coconut_oil

PT coordinator	**Second contact**
Stefanka Bratinova	Lubomir Karasek
Fax: 0032-14-571783 e-mail: jrc-eurl-pah@ec.europa.eu	

Participants are invited to indicate the preferred solvent type of the standard solution (either toluene or acetonitrile) in the Registration Form as well as any justify additional requests.

Distribution of information:
The NRLs are kindly requested to distribute as soon as possible this information and the link to the Registration form to the OCLs under their responsibility, and to assist the EURL in identifying laboratories that are eligible to participate in the study.

Access of NRLs to performance data of official food control laboratories:
Two options:

1) *NRL enrols OCLs and covers participation fee.*
   The NRL submits to the EURL a list of participants including name and address of laboratory, and details of the contact person (name, address - no post box! - email and telephone number). The coverage of the participation fees must be confirmed and details for invoicing (e.g. order number) have to be provided. It shall be made clear, that the full participation fee is payable upon dispatch of the test samples. In return,

the performance data of the respective official food control laboratories will be disclosed to the NRL.

2) The *OCL (identified as such by the respective NRL) enrols itself* in the inter-laboratory comparison *and covers the participation fee*.
   The NRL will get access to performance data of the OCL only upon providing to the EURL for PAHs a letter of consent.

Should you require further clarification, please do not hesitate to contact the EURL team via:

JRC-EURL-PAH@ec.europa.eu

With kind regards,

Stefanka Bratinova

Cc: Hendrik Emons, Lubomir Karasek

ANNEX 3: Registration form

EURL PAH 2016 Proficiency Test on the determination of 4 marker PAHs in coconut oil

Fields marked with * are mandatory.

European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

EURL PAH 2017 PT - PAH in cocout oil - Registration

This inter-laboratory comparison targets the analysis of the 4 EU marker PAHs (benzo[a]pyrene, benz [a]anthracene, benzo[b]fluoranthene, and chrysene) in coconut oil. The set of test samples will be distributed in the second half of January and will consisting of an amber glass ampule containing about 5g of coconut oil.

Results have to be reported for the individual PAHs as well as for the sum of the four PAHs within 4 weeks from sample dispatch.

In addition, a solution of PAHs in solvent will be supplied to participants with disclosed concentration of the analytes, in order to allow participants to verify their instrument calibration. Therefore, results have not to be reported for this material.

Participants are requested to choose either toluene or acetonitrile as solvent for the solution of PAHs in solvent.

This interlaboratory comparison is organised under accreditation to ISO 17043.

Participation is MANDATORY and free of charge for National Reference Laboratories.

The PARTICIPATION FEE is 350 Euro for Official Food Control Laboratories per participation

* Organisation

1

Department

* Address (for DHL shipment)

* City

* Postal code

* Country

* Name of the contact person

*Email

* Telephone (DHL requirement)

* NRL or OCL

- NRL
- OCL

2

Who is the enrolling laboratory (respectively to whom the invoce should be sent)

- enrolled by OCL itself (invoice sent to the abovementioned address)
- enrolled by the respective NRL (invoice sent to the respective NRL)

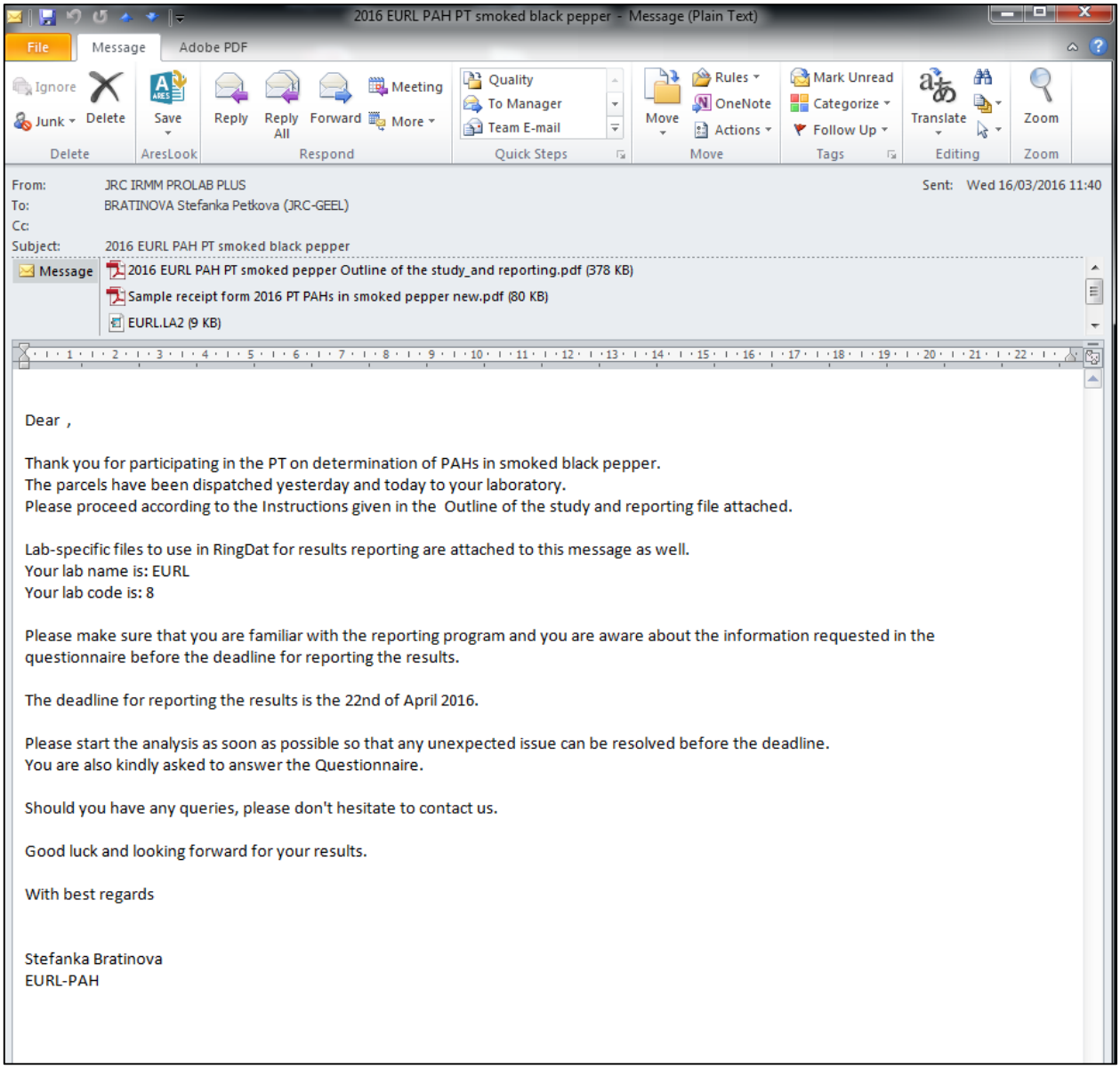
* Prefered solvent for the standard solution

- acetonitrile
- toluene

Any comment or request (not more than 100 characters)

3

ANNEX 4: Announcement of material dispatch



2016 EURL PAH PT smoked black pepper - Message (Plain Text)

File | Message | Adobe PDF

Ignore | Junk | Delete | Save | Reply | Reply All | Forward | Meeting | More | Quality | To Manager | Team E-mail | Move | Rules | OneNote | Actions | Mark Unread | Categorize | Follow Up | Translate | Zoom

Delete | AresLook | Respond | Quick Steps | Move | Tags | Editing | Zoom

From: JRC IRMM PROLAB PLUS
Sent: Wed 16/03/2016 11:40
To: BRATINOVA Stefanka Petkova (JRC-GEEL)
Cc:
Subject: 2016 EURL PAH PT smoked black pepper

Message
2016 EURL PAH PT smoked pepper Outline of the study_and reporting.pdf (378 KB)
Sample receipt form 2016 PT PAHs in smoked pepper new.pdf (80 KB)
EURL.LA2 (9 KB)

Dear ,

Thank you for participating in the PT on determination of PAHs in smoked black pepper.
The parcels have been dispatched yesterday and today to your laboratory.
Please proceed according to the Instructions given in the Outline of the study and reporting file attached.

Lab-specific files to use in RingDat for results reporting are attached to this message as well.
Your lab name is: EURL
Your lab code is: 8

Please make sure that you are familiar with the reporting program and you are aware about the information requested in the questionnaire before the deadline for reporting the results.

The deadline for reporting the results is the 22nd of April 2016.

Please start the analysis as soon as possible so that any unexpected issue can be resolved before the deadline.
You are also kindly asked to answer the Questionnaire.

Should you have any queries, please don't hesitate to contact us.

Good luck and looking forward for your results.

With best regards

Stefanka Bratinova
EURL-PAH

ANNEX 5: Documents sent to participants - OUTLINE and REPORTING INSTRUCTIONS

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE

Directorate F – Health, Consumers and Reference Materials

Geel, 18 January 2017

EURL-PAH 2017 PT- PAHs in coconut oil

Dear Madame/Sir,

The inter-laboratory comparison study organised by the EU-RL PAHs on the determination of four EU marker PAHs in coconut oil starts with the dispatch of the samples.

The target analytes are the four EU marker PAHs (benzo[*a*]pyrene, benzo[*b*]fluoranthene, benz[*a*]anthracene, chrysene) and their sum. The participants are requested to report results on all of them.

Each participant is provided with amber glass vials containing a portion of coconut oil, naturally contaminated with PAHs and a known standard solution in either toluene or acetonitrile for checking of the instrument calibration against an external reference.

Outline of the study.

The participating laboratories shall apply for the analyses a method of their choice.

The laboratories shall report the results by 20th February 2017 at the latest following the instructions provided further on in this document.

The participants are requested to report the results obtained from three replicate analyses. They also have to report a final value for proficiency assessment. Results have to be reported corrected for recovery and the results for proficiency assessment ("final values") have to be accompanied by the respective measurement uncertainty (also for the sum parameter).

Additionally participants are asked to perform compliance assessment according to the CURRENT legislative limits.

Participants are also requested to report together with the results details of the applied analysis method and some method performance characteristics.

Test material and analytes

1. One 5 ml amber vial, labelled as *"EU-RL PAHs PT 2017 Interlaboratory comparison, 4 EU PAHs in coconut oil"* containing approximately 5 g of a naturally contaminated homogenised coconut oil. The analyte content shall be determined in triplicate. The participants have to report to the EU-RL besides the individual results of the replicate analyses also one value, on which they would like their performance to be assessed. This value is called on the reporting file "final value".

If not analysed immediately after receiving, please store the coconut oil sample at room temperature, protected of light.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-eurl-pah@ec.europa.eu

2. Depending on your preference, one ampoule, labelled as "PAH4 in acetonitrile", or "PAH4 in toluene", with about 1 ml of a solution of **4 EU priority PAHs in acetonitrile, respectively toluene**. The analyte concentration of your preferred solution is given in the attached document. The solutions may be used by the participants to check their instrument calibration against an independent reference. Participants do not have to report results for this solution.

Please bear in mind that the solutions **do not contain any internal standard**. The standard solution in acetonitrile contains small amounts of toluene, which stem from the preparation of stock solution from neat materials.

Reporting the results

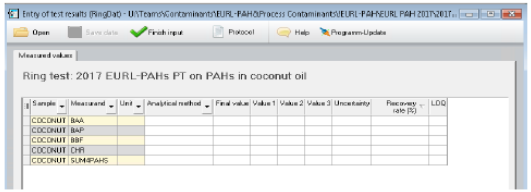
Data generated by the participants will be collected by using software RingDat, supplementary to ProLab software, used until now for professional data handling and statistical analyses of interlaboratory tests results.
You will receive by mail some files for reporting results. You should follow the following instructions:

1. If not available already, please download the data entry program RingDat free from the QuoData web page using following link: http://quodata.de/ringdat_en.php
User: *ringdat*
Password: *prolabdata*

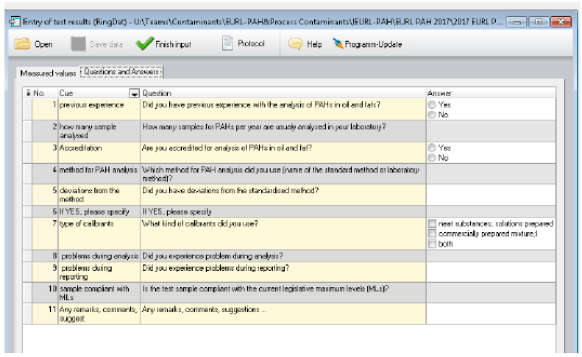
2. Save to the same folder the two lab specific files with the extension **"*.LAB"** and **"*.LA2"**, generated by the ProLab software and provided to each laboratory individually (personal files) by mail.

3. Start the RingDat.exe program and open **"*.LAB"** file for reporting the results. A table will appear with cells for every measurand/sample combination
- the name of each laboratory is codified by the software,
- The **"*.LA2"** file contains information about the participant – laboratory name and laboratory code;
- The **"*.LAB"** file is unique to each laboratory (personal) and contains information about the samples and measurands, that have to be analysed and reported.
- First tab contains the detailed information for the laboratory
- Second tab contains table for entering the results. You could filter the entries by sample or by measurand. The cells marked with red are mandatory to be filled
- Third tab contains a general questionnaire.

4. Fill in the result table with your data.



5. Afterwards, please fill in the questionnaire on the next tab.



6. After finishing the input, save the file using the button on the top menu of the window. You could change the inputs after saving the file as long as you haven't pushed "Finish input" button. At the end finalise the data entry by pushing the "Finish input" button.

7. Send both the **"*.LAB"** and **"*.LA"** files back to us by e-mail on our functional mail box - jrc-eurl-pah@ec.europa.eu

8. If you want to correct some of your entries after finishing the input, you should use the original *.LAB file downloaded from the mail.

In case of questions, please do not hesitate to contact us.

With kind regards,

Stefanka Bratinova
EURL-PAHs

SAMPLE RECEIPT

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate F - Health, Consumers and Reference Materials
Food & Feed Compliance

PROFICIENCY TESTING MATERIAL RECEIPT FORM

2017 PT- PAHs in coconut oil

Contact person	
Affiliation	
City, Country	

Content of the parcel

1. One 5 ml amber glass vial containing about 5 g of coconut oil
2. One 2 ml amber glass ampule, containing about 1 ml of 4 markers PAHs in solvent
3. PAH standard solution specification sheet
4. Solvent safety data sheet
5. One sample receipt form (= this form), which is e-mailed as well to be filed and send electronically

TEST SAMPLES COULD BE STORED AT ROOM TEMPERATURE

Please ensure that the items listed below have been received undamaged, and then describe the relevant statement:

Date of the receipt of the test materials	
All items have been received undamaged	YES ☐ / NO ☐
If NO, please list damaged items	

Please return the completed form to

Stefanka Bratinova

Retiesweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 800. http://irc.ec.europa.eu
Telephone: direct line (32-14) 571 229. Fax: (32-14) 571 3.
E- mail: jrc-EURL-PAH@ec.europa.eu

ANNEX 6: Technical specifications of the calibration solutions

ACETONITRILE SOLUTION

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 24/02/2016

Standard solution specification sheet	**PAH4 in ACETONITRILE**
Date of production: 18/02/2016	Total volume: 1 mL
Expiry date: *August 2016*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/mL)	U** ± %
1	Benz[*a*]anthracene	56-55-3	**64.3**	**50.6**	0.3
2	Benzo[*a*]pyrene	50-32-8	**64.2**	**50.5**	0.4
3	Benzo[*b*]fluoranthene	205-99-2	**64.0**	**50.3**	0.5
4	Chrysene	218-01-9	**64.9**	**51.1**	0.4
5	SUM PAH4		**257.4**	**202.4**	0.9

** The concentrations were calculated taking into account the purity statements of the single products. The concentration values are based on the gravimetrical preparation data.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Acetonitrile:Toluene (m/m 99.4:0.6)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-eurl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

TOLUENE SOLUTION

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
JOINT RESEARCH CENTRE
Directorate D - Institute for Reference Materials and Measurements
European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 24/02/2016

Standard solution specification sheet	**PAH4 in TOLUENE**
Date of production: 18/02/2016	Total volume: 1 mL
Expiry date: *August 2016*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/mL)	U** ± %
1	Benz[*a*]anthracene	56-55-3	**58.0**	**50.3**	0.3
2	Benzo[*a*]pyrene	50-32-8	**57.8**	**50.1**	0.4
3	Benzo[*b*]fluoranthene	205-99-2	**57.6**	**50.0**	0.5
4	Chrysene	218-01-9	**58.5**	**50.7**	0.4
5	SUM PAH4		**232.0**	**201.1**	0.9

** The concentrations were calculated taking into account the purity statements of the single products. The concentration values are based on the gravimetrical preparation data.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Toluene

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

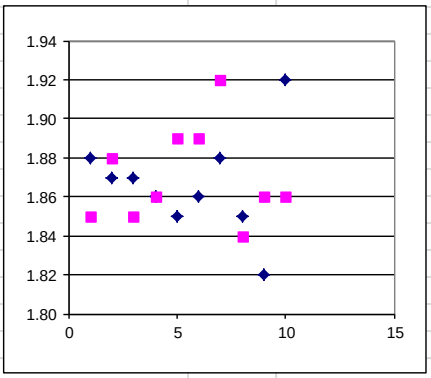
E-mail: jrc-irmm-eurl-pah@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

ANNEX 7: Homogeneity of the coconut oil test material

	n =	10		
	mean =	1.8680	22%	**= σ-trg(%)**
0.00034	**s_x =**	0.01844	0.41096	**= σ-trg**
√MSW =	**s_w =**	0.02324		
sbb=ss	**s_s =**	0.00837	0.12329	**= 0,3*σ**
	ISO-13528	passed		
	F =	1.25926	3.02038	= Fcrit
		passed		
	IUPAC			
	(MSB-MSW)/2	7E-05	0.02912	= F1*(0,3*σ)^2+F2*MSW
		passed		

BAA

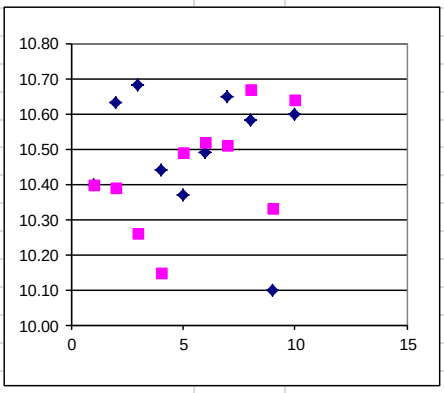
Bottle	Result a	Result b	diff	sum	avg
Ampoule 08	1.88	1.85	0.03	3.73	1.87
Ampoule 14	1.87	1.88	-0.01	3.75	1.88
Ampoule 22	1.87	1.85	0.02	3.72	1.86
Ampoule 39	1.86	1.86	0.00	3.72	1.86
Ampoule 43	1.85	1.89	-0.04	3.74	1.87
Ampoule 54	1.86	1.89	-0.03	3.75	1.88
Ampoule 67	1.88	1.92	-0.04	3.80	1.90
Ampoule 73	1.85	1.84	0.01	3.69	1.85
Ampoule 87	1.82	1.86	-0.04	3.68	1.84
Ampoule 95	1.92	1.86	0.06	3.78	1.89
		Σ(diff)^2 =	0.0108		
		var(sum)/2 =		0.00068	=MSB



	n =	10		
	mean =	10.465	22%	**= σ-trg(%)**
0.01815	**s_x =**	0.13472	2.3023	**= σ-trg**
√MSW =	**s_w =**	0.14415		
sbb=ubb=	**s_s =**	0.08809	0.69069	**= 0,3*σ**
	ISO-13528	passed		
	F =	1.74687	3.02038	= Fcrit
		passed		
	IUPAC			
	(MSB-MSW)/2	0.00776	0.91785	= F1*(0,3*σ)^2+F2*MSW
		passed		

CHR

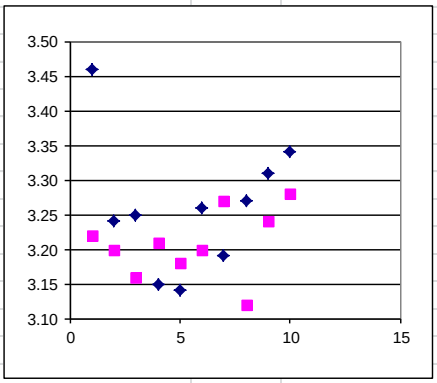
Bottle	Result a	Result b	diff	sum	avg
Ampoule 08	10.40	10.40	0.00	20.80	10.40
Ampoule 14	10.63	10.39	0.24	21.02	10.51
Ampoule 22	10.68	10.26	0.42	20.94	10.47
Ampoule 39	10.44	10.15	0.29	20.59	10.30
Ampoule 43	10.37	10.49	-0.12	20.86	10.43
Ampoule 54	10.49	10.52	-0.03	21.01	10.51
Ampoule 67	10.65	10.51	0.14	21.16	10.58
Ampoule 73	10.58	10.67	-0.09	21.25	10.63
Ampoule 87	10.10	10.33	-0.23	20.43	10.22
Ampoule 95	10.60	10.64	-0.04	21.24	10.62
		Σ(diff)^2 =	0.4156		
		var(sum)/2 =		0.0363	=MSB



	n =	10			
	mean =	3.2345	22%	**= σ-trg(%)**	
0.0033	**s_x =**	0.05742	0.71159	**= σ-trg**	
√MSW =	**s_w =**	0.07533			
sbb=ss	**s_s =**	0.02143	0.21348	**= 0,3*σ**	
	ISO-13528	passed			
	F =	1.16192	3.02038	= Fcrit	
		passed			
	IUPAC				
	(MSB-MSW)/2	0.00046	0.09141	= F1*(0,3*σ)^2+F2*MSW	
		passed			

BBF

Bottle	Result a	Result b	diff	sum	avg
Ampoule 08	3.46	3.22	0.24	6.68	3.34
Ampoule 14	3.24	3.20	0.04	6.44	3.22
Ampoule 22	3.25	3.16	0.09	6.41	3.21
Ampoule 39	3.15	3.21	-0.06	6.36	3.18
Ampoule 43	3.14	3.18	-0.04	6.32	3.16
Ampoule 54	3.26	3.20	0.06	6.46	3.23
Ampoule 67	3.19	3.27	-0.08	6.46	3.23
Ampoule 73	3.27	3.12	0.15	6.39	3.20
Ampoule 87	3.31	3.24	0.07	6.55	3.28
Ampoule 95	3.34	3.28	0.06	6.62	3.31

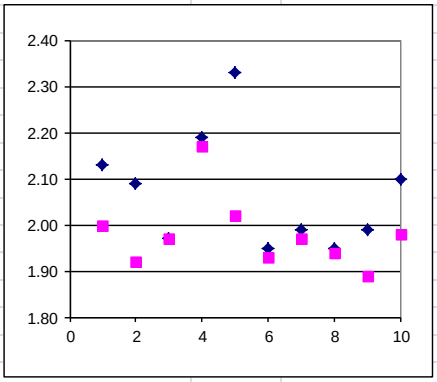


Σ(diff)^2 =	0.1135		
var(sum)/2 =		0.00659	=MSB

	n =	10			
	mean =	2.024	22%	**= σ-trg(%)**	
0.00829	**s_x =**	0.09107	0.44528	**= σ-trg**	
√MSW =	**s_w =**	0.09154			
	s_s =	0.06406	0.13358	**= 0,3*σ**	
	ISO-13528	passed			
	F =	1.97932	3.02038	= Fcrit	
		passed			
	IUPAC				
	(MSB-MSW)/2	0.0041	0.04201	= F1*(0,3*σ)^2+F2*MSW	
		passed			

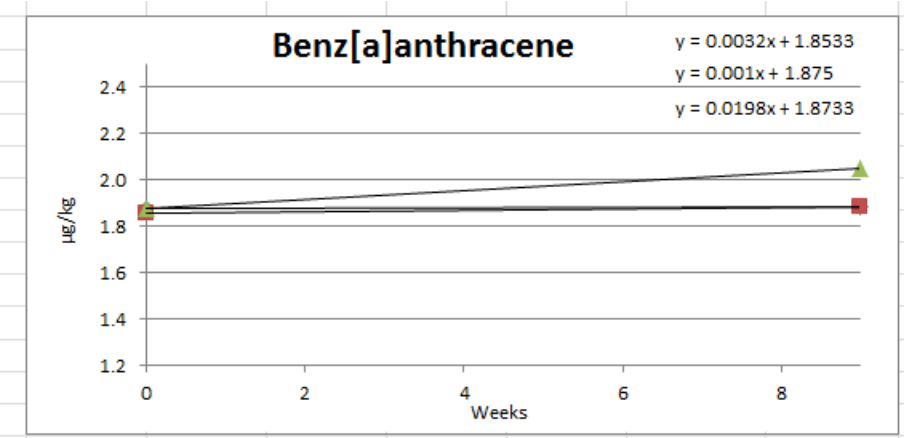
BAP

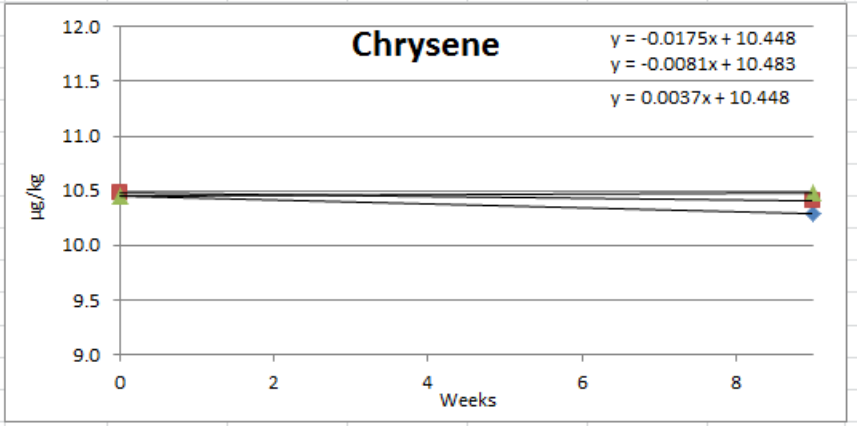
Bottle	Result a	Result b	diff	sum	avg
Ampoule 08	2.13	2.00	0.13	4.13	2.07
Ampoule 14	2.09	1.92	0.17	4.01	2.01
Ampoule 22	1.97	1.97	0.00	3.94	1.97
Ampoule 39	2.19	2.17	0.02	4.36	2.18
Ampoule 43	2.33	2.02	0.31	4.35	2.18
Ampoule 54	1.95	1.93	0.02	3.88	1.94
Ampoule 67	1.99	1.97	0.02	3.96	1.98
Ampoule 73	1.95	1.94	0.01	3.89	1.95
Ampoule 87	1.99	1.89	0.10	3.88	1.94
Ampoule 95	2.10	1.98	0.12	4.08	2.04

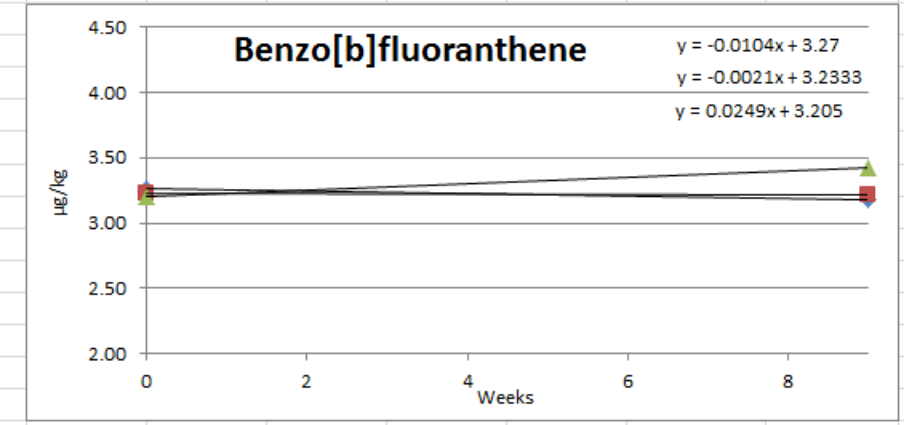


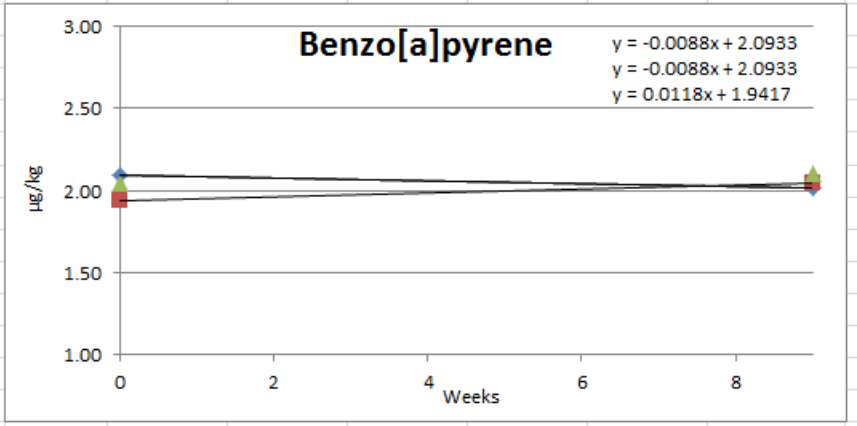
Σ(diff)^2 =	0.1676		
var(sum)/2 =		0.01659	=MSB

ANNEX 8. Stability of the coconut oil test material for the period of the study





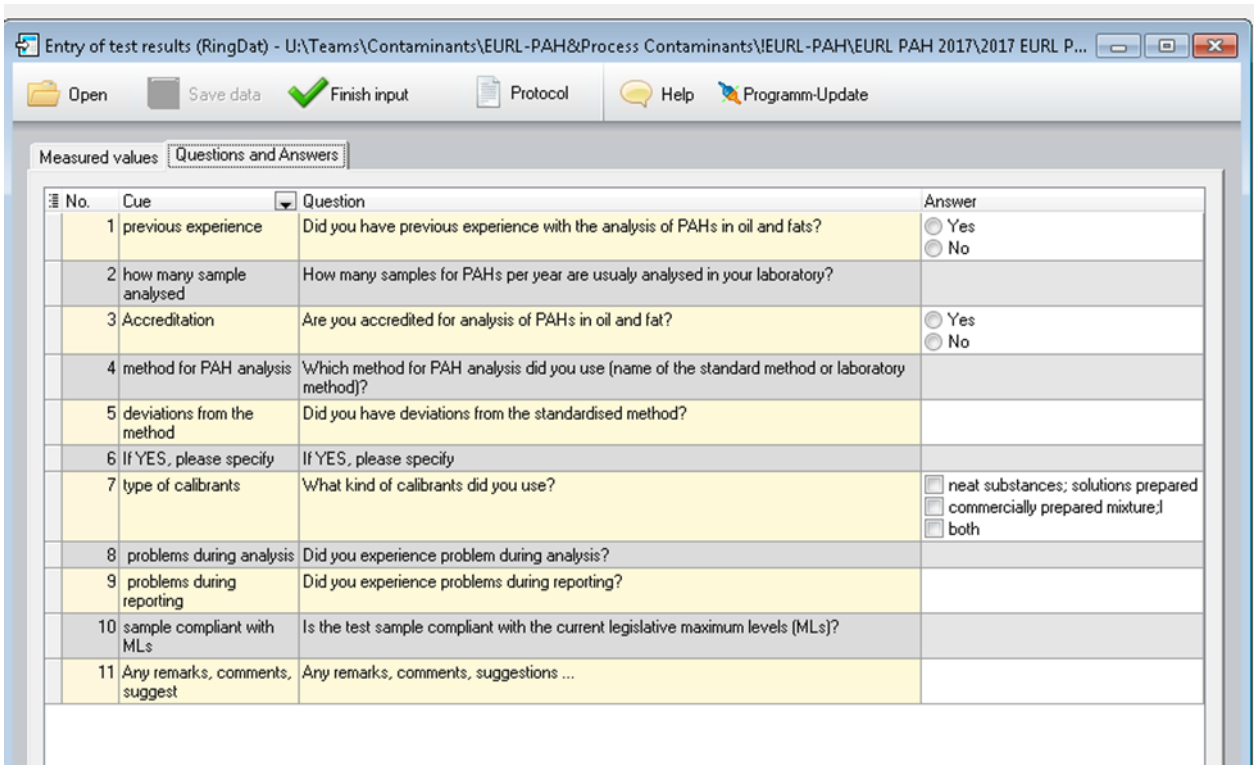




- at room temperature - recommended conditions (~ 20 °C).
- one week at 40°C (simulating transport conditions
- in a deep freezer at the reference conditions - (~ -80 °C).

ANNEX 9. Questionnaire & Answers from participants

No.	Cue	Question	Answers	Edit type
		Click here to define a new question for 2017 EURL-PAHs PT on PAHs in coconut oil.		
Ring test : 2017 EURL-PAHs PT on PAHs in coconut oil (11 questions, 457 answers)				
1	previous experience	Did you have previous experience with the analysis of PAHs in oil and fats?	49 Answers	RadioGroup
2	how many sample analysed	How many samples for PAHs per year are usualy analysed in your laboratory?	47 Answers	TextEdit
3	Accreditation	Are you accredited for analysis of PAHs in oil and fat?	49 Answers	RadioGroup
4	method for PAH analysis	Which method for PAH analysis did you use (name of the standard method or laboratory method)?	49 Answers	TextEdit
5	deviations from the method	Did you have deviations from the standardised method?	39 Answers	TextEdit
6	If YES, please specify	If YES, please specify	12 Answers	TextEdit
7	type of calibrants	What kind of calibrants did you use?	49 Answers	CheckGroup
8	problems during analysis	Did you experience problem during analysis?	48 Answers	TextEdit
9	problems during reporting	Did you experience problems during reporting?	47 Answers	TextEdit
10	sample compliant with MLs	Is the test sample compliant with the current legislative maximum levels (MLs)?	47 Answers	TextEdit
11	Any remarks, comments, suggest	Any remarks, comments, suggestions ...	21 Answers	TextEdit



Lab Code	1. Previous experience	2. How many sample analysed	3. Accreditation	4. Method for PAH analysis	5. Deviations from the method	6. If Yes please specify
10	Yes		Yes	FC094.1		
11	Yes	15-20	Yes	laboratory method	No	
12	Yes	<50	Yes	CEN/TS 16621	No	
13	Yes	50	Yes	HPLC-FLD	Yes	lower sample weight for oil 1 g instead of 1.5 g
14	Yes	Around 10-15 oil or fat samples, 200-250 samples alltogether	Yes	Laboratory method:Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in food by GC-MS - PAH/66/2007	No	
15	Yes	~200	Yes	35 § LMBG 07.00.40:2004 for BAP	Yes	Modified for PAHs
17	Yes	1	Yes	laboratory method	No	
18	Yes	<100	Yes	Extraction by ASE, clean-up GPC + SPE (silica column), GC/MS	weight of sample taken 0,5 g instead of 2,0 g	
19	Yes	80-100	Yes	Laboratory method QMI 132	No	
20	Yes	100	Yes	A-0824 and A-0834	No	
21	Yes	differently 10-100	Yes	Laboratory method	Yes	We use 2 g sample for analysis, due to the little amount of sample we use 1 g sample
22	Yes	30	Yes	03-02 PAHs-GC-MS/ HPLC Determination of Polycyclic Aromatic Hydrocarbons in Food based on ISO 15753:2006	No	
23	Yes	15	Yes	GPC-SPE and GC-MS	No	
24	Yes	50	Yes	Food analysis - Determination of benzo[a]pyrene, benz[a]anthracene, chrysene and benzo[b]fluoranthene in foodstuffs by high performance liquid chromatography with fluorescence detection (HPLC-FD)	No	
25	Yes	approx. 100	Yes	Single-laboratory validation of a GC/MS method for the	Yes	Significantly less sample had to be taken for analysis due to insufficient quantity of test material being supplied. See remarks section.
26	Yes	15	No	In-house method	No	
27	Yes	100	Yes	in house method	No	
28	Yes		Yes	EN 16619:2015	No	
30	Yes	<50	Yes	Laboratory method		
31	Yes	350	Yes	GC/MS EN 16619:2015	Yes	used isotopic internal standard D12 instead of C13
32	Yes	around 30	Yes	SLV-m097.f	No	
33	Yes	500	Yes	Laboratory method	No	
34	Yes	10	Yes	Internal method based on an article		
35	Yes	100	Yes	Determination of PAHs in food by GC-MS	No	
36	Yes	50	Yes	in-house method	/	/
37	Yes	200	Yes	edible oil with GPC and HPLC-FLD	No	
51	Yes	>1000	Yes	VDLUFA VII, 3.3.3.2,1		
52	Yes	>50	Yes	laboratory method		
53	Yes	1600	No	In accordance with ISO 22959	No	
54	Yes	140	Yes	laboratory method	Yes	(Laberca) French LNR method
55	Yes	75	Yes	LABERCA/HAP-TMA.1.06	Yes	recovery volume of 15µL (instead of 20µL) and injection volume of 3µL (instead of 2µL)
56	Yes	55	Yes	DIN EN 16619	Yes	reducing sample weight
57	Yes	50	Yes	ONR CEN/TS 16621 2014 06 01	No	
58	Yes	20	Yes	internal method		
59	Yes	150	Yes	Laboratory method	No	
60	Yes	20	Yes	Internal method	Yes	Sample weight should be 2.5 g but I reduced it in order to have three replicate analysis. I proportionally reduced also the amount of solvent used to dilute the oil.
61	Yes	approx. 120	Yes	saponification, liquid-liquid-extraction, gel permeation chromatography, GC-MS		
62	Yes	60	Yes	POS CHI 058	N.A.	
63	Yes	100	Yes	laboratory method		
64	Yes	>3500	Yes	ISO 22959	Yes	Additional internal standard
65	Yes	30	Yes	LABERCA/HAP-al.1.05	No	
66	Yes	100	No	QuEChERS (laboratory method)	No	
67	Yes	150	Yes	laboratory method	No	
68	Yes	1000	Yes	in house method	No	
69	Yes	>20000	Yes	internal method		
70	No	0	No	-	-	-
71	Yes	4000	Yes	internal method : MOC3/28	No	
72	Yes	300	Yes	HPLC-FLD, clean-up with GPC		
73	Yes	60	Yes	LABERCA/HAP-al.1	No	

Lab Code	7.Type of calibrants	8. Problems during analysis	9. Problems during reporting
10	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	Yes. Not possible to choose a method for SUM4PAHS and thereby Not able to "Finish input"
11	Commercialy prepared mixture	No	No
12	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
13	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
14	Commercialy prepared mixture	No	No, except the 'Finish input' problem you already kNow about.
15	Neat substancws; Solution prepared inhouse	Yes - Not eNough sample for triplicate analysis	Yes
17	Neat substancws; Solution prepared inhouse	No	No
18	Neat substancws; Solution prepared inhouse	-	-
19	Neat substancws; Solution prepared inhouse	No	No
20	Commercialy prepared mixture	No	Yes, box analytical method sum4PAHs could No be filled in
21	Commercialy prepared mixture	This analysis should be repeated, but it was too little sample for the next analysis	No
22	Commercialy prepared mixture	Interferance in BaP was Not very obvious after the first treatment. An additional clean up has been performed by using NH2 columns.	There is No LOD for the SUM, but is equested. There is No option to insert the method used in SUM although it is requested.
23	Commercialy prepared mixture	No	Yes
24	Commercialy prepared mixture		
25	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	Yes - LODs compromised due to low sample mass taken.
26	Neat substancws; Solution prepared inhouse	No	No
27	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
28	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
30	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	Yes
31	Commercialy prepared mixture	No	No
32	Commercialy prepared mixture	No	No
33	Commercialy prepared mixture	No	Not possible to fill in Analytical method for the sum of PAHs
34	Commercialy prepared mixture	No	No
35	Commercialy prepared mixture	No	Yes could Not finish imput.
36	Commercialy prepared mixture	Yes - (1) Not eNough sample material; (2) accident during extraction	No
37	Commercialy prepared mixture	No	Yes analytical method PAK4
51	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
52		No	
53	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	Yes, No analytical method selection possible for the PAH sum. Therefore Noticiation done by the system
54	Commercialy prepared mixture	No	No
55	Commercialy prepared mixture	No	No
56	Commercialy prepared mixture	No	No
57	Commercialy prepared mixture	No	No
58	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
59	Commercialy prepared mixture	No	No
60	Commercialy prepared mixture	No	No
61	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
62	Neat substancws; Solution prepared inhouse	No	Yes
63	Commercialy prepared mixture	No	Yes
64	Commercialy prepared mixture	No	No
65	Commercialy prepared mixture	No	No
66	Neat substancws; Solution prepared inhouse	No	Yes
67	Commercialy prepared mixture	too little material for a triple analysis	No
68	Commercialy prepared mixture	No	No
69	Neat substancws; Solution prepared inhouse/ Commercialy prepared mixture	No	No
70	Neat substancws; Solution prepared inhouse	low recover	Yes
71	Commercialy prepared mixture	No	No
72	Commercialy prepared mixture	interference with the BAP-Peak by the commly used chromatography with PAK Eclipse	No
73	Commercialy prepared mixture	No	No

Lab Code	10. Sample compliant with MLs	11. Any remarks comments suggest
10	Yes	
11	compliant for both sum and BaP	No
12	Yes (2,19 µg/kg - 0,22 µg/kg (U) = 1,97 µg/kg)	
13	No	
14	Yes	
15	Yes	
17	Yes, the sample is compliant with the current legislation	
18	compliant	-
19	No	
20	Yes, the test sample complies taking into account the measurement uncertainty.	No
21	Yes	Sample amount should allow to repeat the analysis
22	Yes	
23	No	No recovery rate are in my sheet
24	No	
25	Yes	The sample size of 5g to be analysed in triplicate is likely to be unrepresentative of the amount of sample received for official control suggested in COMMISSION REGULATION (EU) No 836/2011. Other PT providers distribute adequate amount of test material and only require one result. Please consider sending more of this sample type in future.
26	Yes	
27	No	
28	Yes	
30	Yes	
31	No	
32	Yes	
33	No	
34	No	
35	Yes	
36	Yes	/
37	compliant	
51	Yes	
52	Yes	
53	No, Not for BaP	No
54	Yes	No
55	Yes	The test sample is compliant with the current legislative maximum levels as we performed 3 different analysis and that both of mean values of BaP and of the sum of 4 HAPs minus the uncertainty are lower than the MLs.
56	Yes. We detected 222 µg/kg of BAP and 1821 µg/kg of sum of 4PAH in the sample. ML for BAP is 20 µg/kg and ML for the sum of 4PAH is 20 µg/kg in coconut oil (VO(EU)1881/2006). The result of BAP exceeds the ML but considering the measurement uncertainty of 20% the result is below the ML so the sample is compliant to EU legislation.	-
57	No	
58	Yes	No
59	Yes	
60	Yes	No
61	Yes (taking into account and substract measurement uncertainty)	No
62	Yes	No
63		
64	No	-
65	Yes	No
66	No	No
67	No	because of the little material it was Not possible to create a third value
68	Yes	No
69		
70	No	-
71	Yes	
72	Yes (with consideration the Uncertainty for BaP)	
73	Yes	

Annex 10. Method performance LOD and LOQ as reported, μg/kg

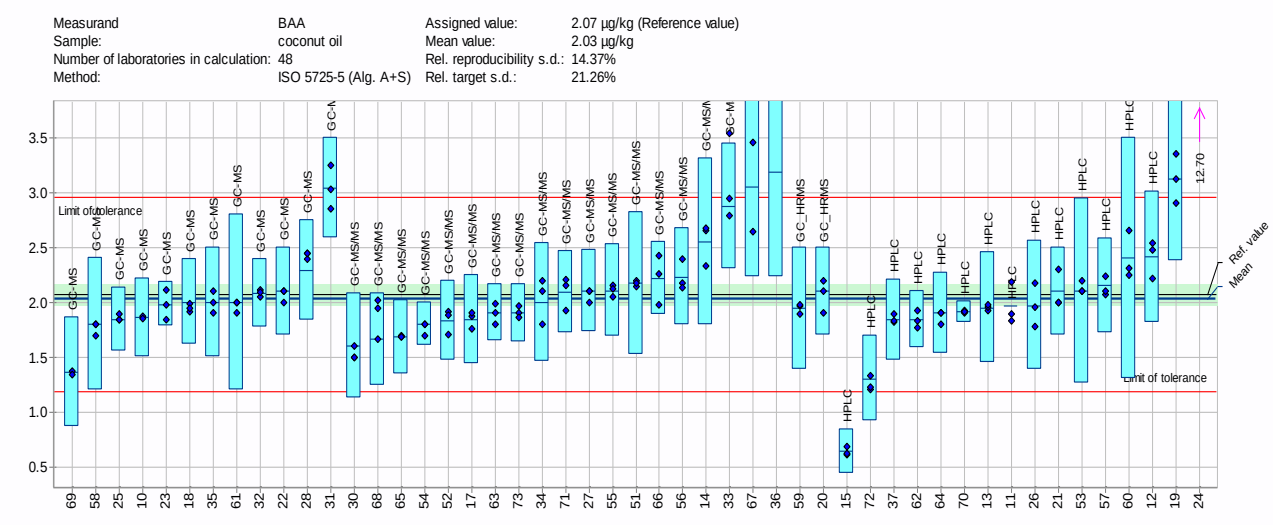
	BAA		BAP		BBF		CHR		Analytical method
Lab code	DL	QL	DL	QL	DL	QL	DL	QL	
	0.10	0.20	0.1	0.3	0.1	0.3	0.1	0.3	GC-MS
11	0.20	0.40	0.2	0.4	0.2	0.4	0.2	0.4	HPLC
10	0.01	0.58	0.01	0.58	0.03	0.58	0.03	0.58	HPLC
13	0.03	0.05	0.03	0.05	0.05	0.1	0.03	0.05	HPLC
14	0.23	0.75	0.27	0.85	0.28	0.84	0.24	0.75	GC-MS/MS
15	0.06	0.20	0.06	0.2	0.06	0.2	0.2	0.5	HPLC
16									
17	0.02	0.06	0.02	0.06	0.02	0.06	0.02	0.06	GC-MS/MS
18	0.10	0.30	0.1	0.3	0.1	0.3	0.1	0.3	GC-MS
19	0.33	1.00	0.33	1	0.33	1	0.33	1	HPLC
20	0.00	0.01	0.01	0.02	0.01	0.02	0.01	0.02	GC_HRMS
21	0.25	0.50	0.08	0.16	0.2	0.4	0.4	0.8	HPLC
22	0.30	0.90	0.3	0.9	0.3	0.9	0.3	0.9	GC-MS
23	0.10	0.30	0.2	0.6	0.2	0.6	0.1	0.3	GC-MS
24	0.04	0.13	0.04	0.12	0.07	0.13	0.04	0.17	HPLC
25	0.06	0.06	0.36	0.36	0.23	0.23	0.22	0.22	GC-MS
26	0.14	0.47	0.13	0.44	0.1	0.34	0.11	0.37	HPLC
27	0.50	0.30	0.5	0.3	0.5	0.3	0.5	0.3	GC-MS/MS
28	0.20	0.50	0.2	0.5	0.2	0.5	0.2	0.5	GC-MS
29									
30	0.73	0.24	0.73	0.24	0.73	0.24	0.73	0.24	GC-MS/MS
31	0.15	0.45	0.2	0.6	0.2	0.6	0.15	0.45	GC-MS
32	0.10	0.30	0.1	0.3	0.1	0.3	0.1	0.3	GC-MS
33	0.03	0.10	0.03	0.1	0.03	0.1	0.03	0.1	GC-MS/MS
34	0.28	0.80	0.28	0.8	0.28	0.8	0.28	0.8	GC-MS/MS
35	0.30	0.90	0.3	0.9	0.3	0.9	0.3	0.9	GC-MS
36	0.10	0.30	0.1	0.3	0.1	0.3	0.1	0.3	GC-MS/MS
37	0.07	0.21	0.08	0.24	0.15	0.45	0.04	0.12	HPLC
51	0.30	1.00	0.3	0.9	0.3	1	0.3	1	GC-MS/MS
52	0.10	0.05	0.1	0.05	0.1	0.05	0.1	0.05	GC-MS/MS
53	0.02	0.10	0.01	0.1	0.04	0.1	0.04	0.1	HPLC
54	0.03	0.10	0.03	0.1	0.03	0.1	0.03	0.1	GC-MS/MS
55	0.06	0.06	0.1	0.1	0.09	0.09	0.11	0.11	GC-MS/MS
56	0.02	0.05	0.02	0.05	0.02	0.05	0.02	0.05	GC-MS/MS
57	0.51	1.01	0.51	1.01	0.51	1.01	0.51	1.01	HPLC
58	0.30	0.90	0.3	0.9	0.3	0.9	0.3	0.9	GC-MS
59	0.25	0.50	0.25	0.5	0.25	0.5	0.25	0.5	GC_HRMS
60	0.03	0.40	0.01	0.4	0.01	0.4	0.02	0.4	HPLC
61	0.10	0.30	0.1	0.3	0.2	0.5	0.2	0.5	GC-MS
62	0.20	0.50	0.07	0.2	0.2	0.5	0.1	0.5	HPLC
63	0.24	0.45	0.12	0.24	0.24	0.51	0.31	0.49	GC-MS/MS
64	0.08	0.40	0.02	0.1	0.02	0.1	0.08	0.4	HPLC
65	0.10	0.20	0.1	0.2	0.1	0.2	0.1	0.2	GC-MS/MS
66	0.29	0.90	0.29	0.9	0.16	0.52	0.22	0.74	GC-MS/MS
67	0.30	0.90	0.3	0.9	0.3	0.9	0.3	0.9	GC-MS/MS
68	0.50	1.00	0.5	1	0.5	1	0.5	1	GC-MS/MS
69	0.20	0.50	0.2	0.5	0.2	0.5	0.2	0.5	GC-MS
70	0.05	0.10	0.05	0.1	0.05	0.1	0.05	0.1	HPLC
71	0.25	0.50	0.25	0.5	0.25	0.5	0.25	0.5	GC-MS/MS
72	0.30	0.90	0.3	0.9	0.3	0.9	0.3	0.9	HPLC
73	0.10	0.10	0.1	0.1	0.10	0.10	0.1	0.1	GC-MS/MS

ANNEX 11: Data reported by participants

The data reported by the participants are compiled in the following tables. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Red lines indicate the thresholds for satisfactory z-scores. "Mean values" and "Rel. reproducibility s.d." represent the robust mean values and the robust relative standard deviations of the participants data, calculated according to the ISO 13528 algorithm (ISO 5725-5, Algorithm A+S). Very slight differences in the mean values on both graphs below are possible, as on the Kernel density plot the mean values are calculated based on the "final values" reported by the participants while on the distribution of the individual results graphs, they are calculated based on the three replicate results.

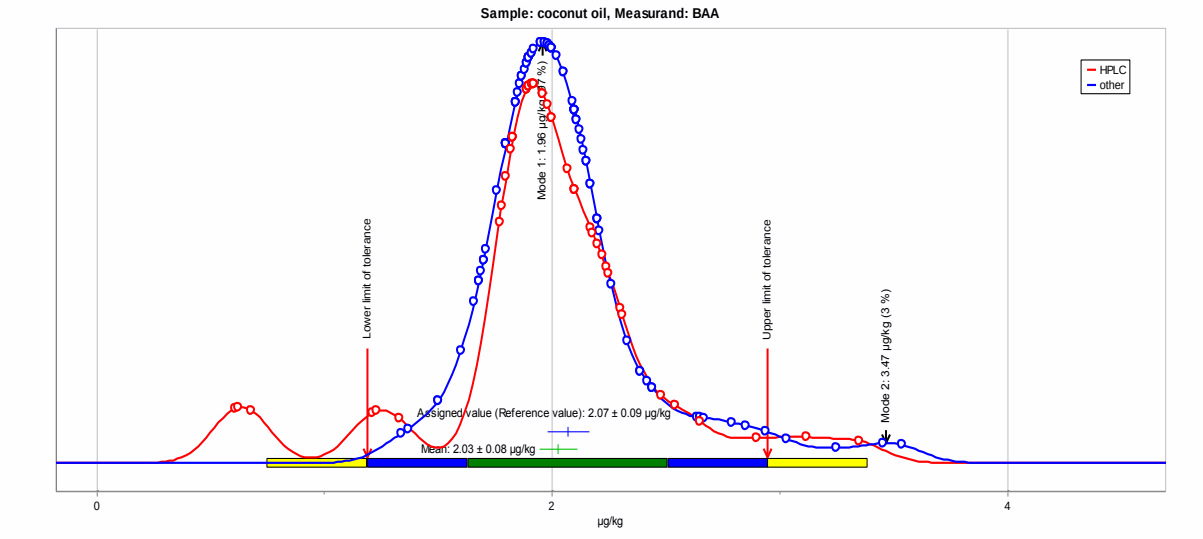
Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content of the coconut oil test sample

blue rombus: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range; green band: confidence interval of the assigned value



Kernel density plot of the reported values for proficiency assessment for the benz[*a*]anthracene (BAA) content of the coconut oil test sample

Red dots and line - HPLC results; blue dots and lines - GC-mass spectrometry results



Results, as reported by the participants and scoring, for the content of benz[*a*]anthracene (BAA) of the coconut oil test sample.

Due to a software problem, the reported significant zeros after the comas are missing

Lab code	M 1	M 2	M 3	X lab	U lab	k	Analytical method	u lab	Z-Score	Zeta score	Classification
10	1.87	1.85		1.86	0.36	2	GC-MS	0.18	-0.5	-1.1	a
11	1.89	2.18	1.83	1.97		2	HPLC		-0.2		
12	2.22	2.48	2.54	2.41	0.6	2	HPLC	0.3	0.8	1.1	a
13	1.92	1.96	1.98	1.95	0.51	2	HPLC	0.26	-0.3	-0.5	a
14	2.65	2.33	2.67	2.55	0.76	2	GC-MS/MS	0.38	1.1	1.3	a
15	0.68	0.61	0.62	0.64	0.2	2	HPLC	0.1	-3.3	-13	a
16						2					
17	1.87	1.9	1.76	1.84	0.41	2	GC-MS/MS	0.21	-0.5	-1.1	a
18	1.99	1.91	1.95	2	0.39	2	GC-MS	0.2	-0.2	-0.3	a
19	3.35	2.9	3.12	3.12	0.75	2	HPLC	0.37	2.4	2.8	a
20	2.2	1.9	2.1	2.1	0.4	2	GC_HRMS	0.2	0.1	0.1	a
21	2	2	2.3	2.1	0.4	2	HPLC	0.2	0.1	0.1	a
22	2	2.1	2.1	2.1	0.4	2	GC-MS	0.2	0.1	0.1	a
23	1.84	2.11	1.98	1.98	0.2	2	GC-MS	0.1	-0.2	-0.8	a
24	12.48	12.84	12.78	12.7	0.44	2	HPLC	0.22	24.2	46.9	a
25	1.84	1.84	1.89	1.84	0.29	2	GC-MS	0.15	-0.5	-1.5	a
26	1.96	1.78	2.17	1.97	0.59	2	HPLC	0.29	-0.2	-0.3	a
27	2.1	2	2.1	2.1	0.38	2	GC-MS/MS	0.19	0.1	0.2	a
28	2.39	2.44	2.44	2.29	0.46	2	GC-MS	0.23	0.5	0.9	a
29						2					
30	1.6	1.5	1.5	1.6	0.48	2	GC-MS/MS	0.24	-1.1	-1.9	a
31	3.25	2.85	3.03	3.04	0.46	2	GC-MS	0.23	2.2	4.1	a
32	2.05	2.11	2.09	2.08	0.31	2	GC-MS	0.16	0	0.1	a
33	3.54	2.79	2.94	2.87	0.57	2	GC-MS/MS	0.29	1.8	2.8	a
34	1.8	2.1	2.2	2	0.54	2	GC-MS/MS	0.27	-0.2	-0.3	a
35	2.1	2	1.9	2	0.5	2	GC-MS	0.25	-0.2	-0.3	a
36				3.18	0.95	2	GC-MS/MS	0.48	2.5	2.3	c
37	1.82	1.89	1.83	1.84	0.37	2	HPLC	0.18	-0.5	-1.2	a
51	2.2	2.14	2.17	2.17	0.65	2	GC-MS/MS	0.33	0.2	0.3	a
52	1.91	1.71	1.88	1.83	0.37	2	GC-MS/MS	0.18	-0.5	-1.3	a
53	2.2	2.1	2.1	2.1	0.84	2	HPLC	0.42	0.1	0.1	a
54	1.8	1.7	1.8	1.8	0.2	2	GC-MS/MS	0.1	-0.6	-2.5	a
55	2.05	2.15	2.12	2.11	0.42	2	GC-MS/MS	0.21	0.1	0.2	a
56	2.39	2.17	2.13	2.23	0.45	2	GC-MS/MS	0.22	0.4	0.7	a
57	2.07	2.24	2.1	2.15	0.43	2	HPLC	0.21	0.2	0.4	a
58	1.7	1.8	1.8	1.8	0.6	2	GC-MS	0.3	-0.6	-0.9	a
59	1.97	1.98	1.89	1.94	0.56	2	GC_HRMS	0.28	-0.3	-0.5	a
60	2.65	2.31	2.25	2.4	1.1	2	HPLC	0.55	0.8	0.6	c
61	2	2	1.9	2	0.8	1	GC-MS	0.8	-0.2	-0.1	c
62	1.83	1.77	1.92	1.84	0.26	2	HPLC	0.13	-0.5	-1.7	a
63	1.9	1.99	1.8	1.9	0.26	2	GC-MS/MS	0.13	-0.4	-1.2	a
64	1.9	1.8	1.9	1.9	0.37	2	HPLC	0.18	-0.4	-0.9	a
65	1.69	1.68	1.68	1.68	0.34	2	GC-MS/MS	0.17	-0.9	-2.2	a
66	2.26	2.42	1.98	2.22	0.33	2	GC-MS/MS	0.17	0.3	0.9	a
67	3.45	2.64		3.05	0.82	2	GC-MS/MS	0.41	2.2	2.4	a
68	1.66	1.95	2.02	1.66	0.42	2	GC-MS/MS	0.21	-0.9	-1.9	a
69	1.37	1.34		1.36	0.5	2	GC-MS	0.25	-1.6	-2.8	a
70	1.9	1.92	1.91	1.91	0.1	2	HPLC	0.05	-0.4	-2.4	a
71	1.92	2.15	2.21	2.09	0.38	2	GC-MS/MS	0.19	0	0.1	a
72	1.33	1.21	1.23	1.3	0.39	2	HPLC	0.2	-1.8	-3.8	a
73	1.9	1.97	1.86	1.9	0.27	2	GC-MS/MS	0.13	-0.4	-1.2	a

Satisfactory, Questionable, **Unsatisfactory**

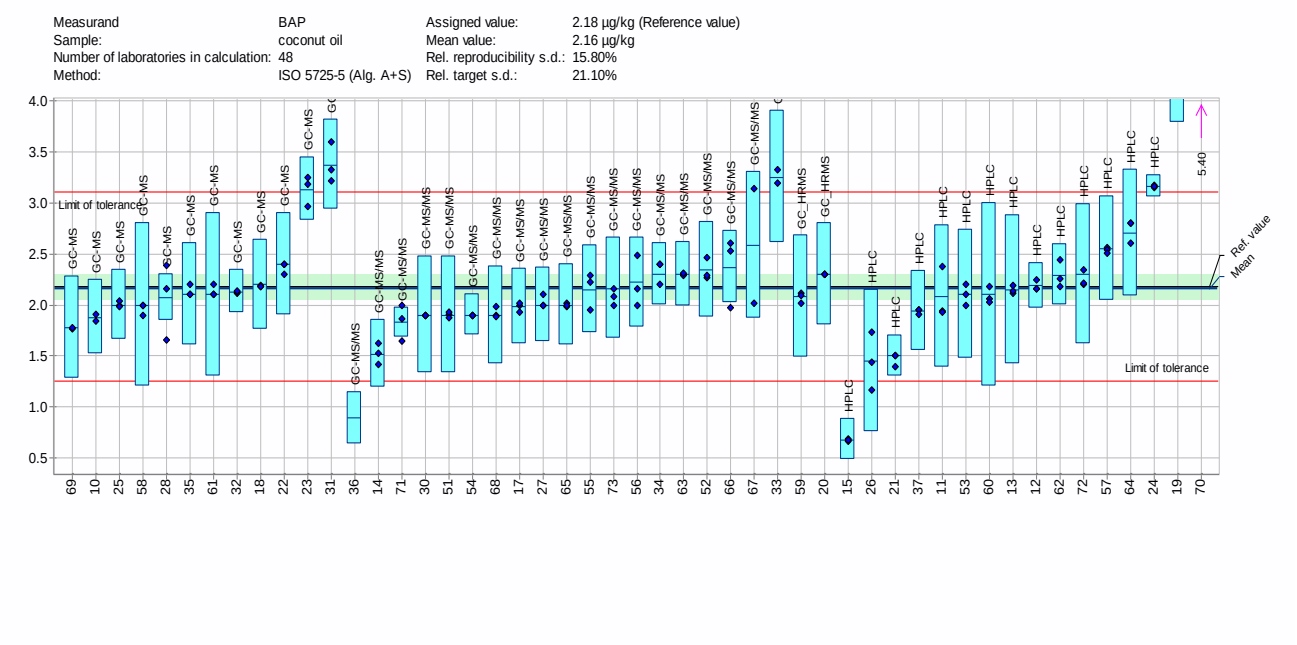
a : $u_{ref} \leq u_{lab} \leq u_{max}$ (σ_p);

b : $u_{lab} < u_{ref}$;

c : $u_{lab} > u_{max}$ (σ_p)

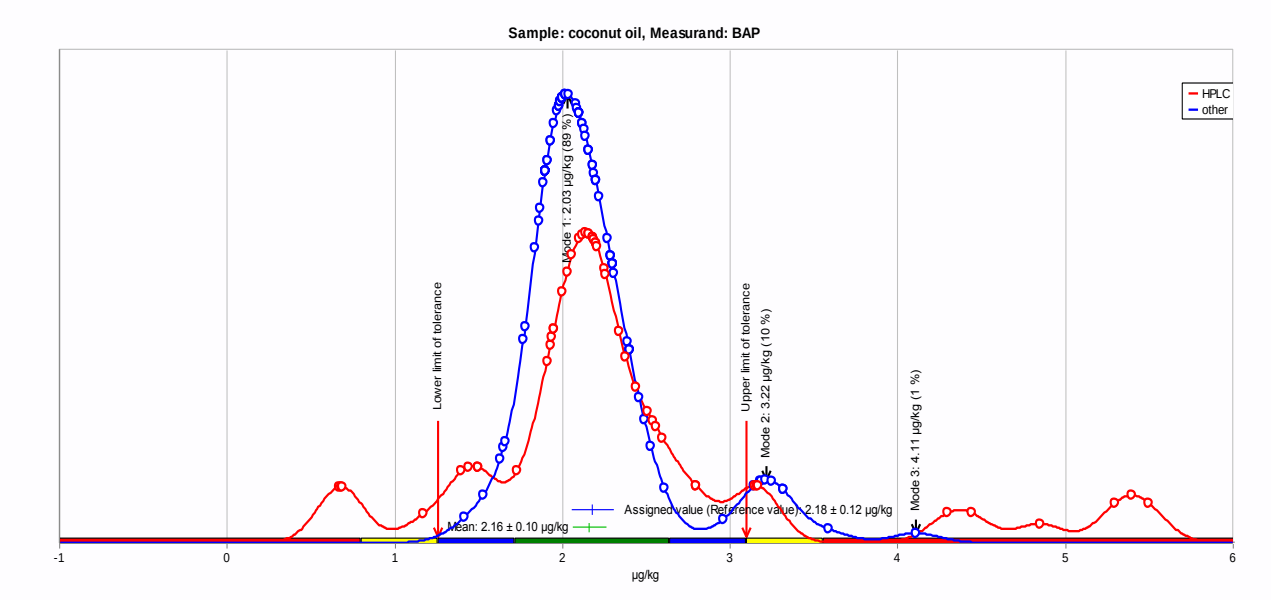
Distribution of individual results of replicate determinations reported for the benzo[*a*] pyrene (BAP) content of the coconut oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the benzo[*a*]pyrene (BAP) content of the coconut oil test sample

Red dots and line - HPLC results; blue dots and lines - GC-mass spectrometry results



Results, as reported by the participants, for the content of benzo[*a*]pyrene (BAP) of the coconut oil test sample.

Due to a software problem, the reported significant zeros after the comas are missing

Lab code	M 1	M 2	M 3	X lab	U lab	k	Analytical method	u lab	Z-Score	Zeta score	Classification
10	1.91	1.84		1.88	0.37	2	GC-MS	0.18	-0.7	-1.6	a
11	2.38	1.94	1.93	2.08	0.7	2	HPLC	0.35	-0.2	-0.3	a
12	2.25	2.16	2.16	2.19	0.22	2	HPLC	0.11	0	0.1	a
13	2.12	2.14	2.19	2.15	0.73	2	HPLC	0.36	-0.1	-0.1	a
14	1.53	1.42	1.63	1.52	0.33	2	GC-MS/MS	0.17	-1.4	-3.8	a
15	0.67	0.69	0.68	0.68	0.2	2	HPLC	0.1	-3.3	-12.9	a
16						2					
17	1.93	1.99	2.02	1.98	0.37	2	GC-MS/MS	0.19	-0.4	-1	a
18	2.19	2.18	2.18	2.2	0.44	2	GC-MS	0.22	0	0.1	a
19	4.85	4.44	4.3	4.53	0.75	2	HPLC	0.38	5.1	6.2	a
20	2.3	2.3	2.3	2.3	0.5	2	GC_HRMS	0.25	0.3	0.5	a
21	1.5	1.4	1.5	1.5	0.2	2	HPLC	0.1	-1.5	-5.8	a
22	2.3	2.4	2.4	2.4	0.5	2	GC-MS	0.25	0.5	0.9	a
23	2.96	3.25	3.18	3.13	0.31	2	GC-MS	0.16	2.1	5.7	a
24	3.15	3.17	3.16	3.16	0.11	2	HPLC	0.06	2.1	12	b
25	2	2.04	1.98	2	0.34	2	GC-MS	0.17	-0.4	-1	a
26	1.44	1.17	1.73	1.45	0.7	2	HPLC	0.35	-1.6	-2.1	a
27	2	2.1	2	2	0.36	2	GC-MS/MS	0.18	-0.4	-0.9	a
28	2.39	1.66	2.16	2.07	0.23	2	GC-MS	0.11	-0.2	-0.8	a
29						2					
30	1.9	1.9	1.9	1.9	0.57	2	GC-MS/MS	0.28	-0.6	-1	a
31	3.21	3.32	3.59	3.37	0.44	2	GC-MS	0.22	2.6	5.2	a
32	2.12	2.13	2.14	2.13	0.21	2	GC-MS	0.11	-0.1	-0.4	a
33	4.11	3.19	3.32	3.25	0.65	2	GC-MS/MS	0.33	2.3	3.2	a
34	2.2	2.4	2.4	2.3	0.3	2	GC-MS/MS	0.15	0.3	0.7	a
35	2.2	2.1	2.1	2.1	0.5	2	GC-MS	0.25	-0.2	-0.3	a
36				0.89	0.26	2	GC-MS/MS	0.13	-2.8	-9	a
37	1.95	1.95	1.91	1.94	0.39	2	HPLC	0.2	-0.5	-1.2	a
51	1.91	1.87	1.93	1.9	0.57	2	GC-MS/MS	0.28	-0.6	-1	a
52	2.27	2.46	2.29	2.34	0.47	2	GC-MS/MS	0.23	0.3	0.7	a
53	2.2	2.1	2	2.1	0.63	2	HPLC	0.32	-0.2	-0.2	a
54	1.9	1.9	1.9	1.9	0.2	2	GC-MS/MS	0.1	-0.6	-2.4	a
55	2.29	2.22	1.95	2.15	0.43	2	GC-MS/MS	0.22	-0.1	-0.1	a
56	2.49	2.16	2	2.22	0.44	2	GC-MS/MS	0.22	0.1	0.2	a
57	2.56	2.54	2.51	2.55	0.51	2	HPLC	0.26	0.8	1.4	a
58	2	1.9	2	2	0.8	2	GC-MS	0.4	-0.4	-0.4	a
59	2.12	2.09	2.02	2.08	0.6	2	GC_HRMS	0.3	-0.2	-0.3	a
60	2.06	2.03	2.18	2.1	0.9	2	HPLC	0.45	-0.2	-0.2	a
61	2.1	2.2	2.1	2.1	0.8	1	GC-MS	0.8	-0.2	-0.1	c
62	2.26	2.18	2.44	2.29	0.3	2	HPLC	0.15	0.2	0.7	a
63	2.3	2.29	2.31	2.3	0.32	2	GC-MS/MS	0.16	0.3	0.7	a
64	2.8	2.6	2.8	2.7	0.62	2	HPLC	0.31	1.1	1.6	a
65	1.98	2.02	2	2	0.4	2	GC-MS/MS	0.2	-0.4	-0.9	a
66	2.61	2.53	1.97	2.37	0.36	2	GC-MS/MS	0.18	0.4	1	a
67	3.14	2.02		2.58	0.72	2	GC-MS/MS	0.36	0.9	1.1	a
68	1.9	1.89	1.98	1.9	0.48	2	GC-MS/MS	0.24	-0.6	-1.1	a
69	1.77	1.78		1.77	0.5	2	GC-MS	0.25	-0.9	-1.6	a
70	5.4	5.5	5.3	5.4	0.1	2	HPLC	0.05	7	41.2	b
71	1.65	1.86	1.99	1.83	0.15	2	GC-MS/MS	0.07	-0.8	-3.7	a
72	2.34	2.2	2.21	2.3	0.69	2	HPLC	0.34	0.3	0.3	a
73	2.16	2	2.08	2.16	0.5	2	GC-MS/MS	0.25	0	-0.1	a

Satisfactory, Questionable, **Unsatisfactory**

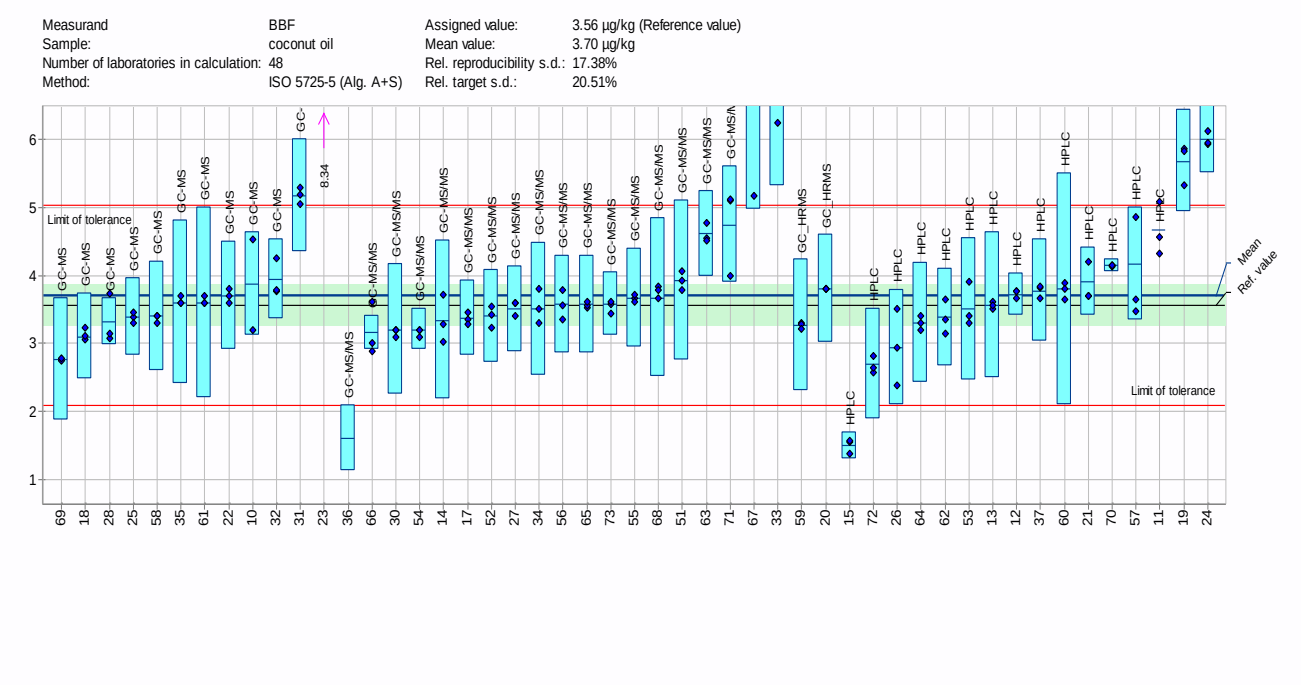
a : $u_{ref} \leq u_{lab} \leq u_{max}$ (σ_p);

b : $u_{lab} < u_{ref}$;

c : $u_{lab} > u_{max}$ (σ_p)

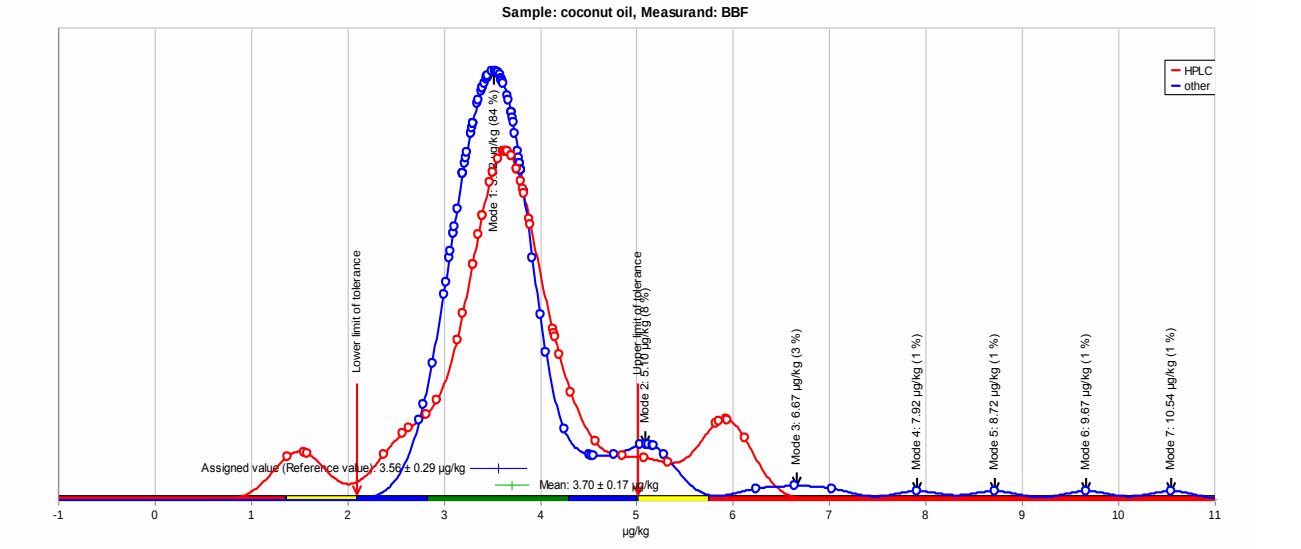
Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content of the coconut oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the benzo[*b*]fluoranthene (BBF) content of the coconut oil test sample

Red dots and line - HPLC results; blue dots and lines - GC-mass spectrometry results



Results, as reported by the participants, for the content of benzo[*b*]-fluoranthene (BBF) of the coconut oil test sample.

Due to a software problem, the reported significant zeros after the comas are missing

Lab code	M 1	M 2	M 3	X lab	U lab	k	Analytical method	u lab	Z-Score	Zeta score	Classification
10	4.53	3.2		3.87	0.76	2	GC-MS	0.38	0.4	0.8	a
11	5.08	4.57	4.32	4.66		2	HPLC		1.5		
12	3.76	3.76	3.66	3.72	0.31	2	HPLC	0.15	0.2	0.8	a
13	3.62	3.51	3.56	3.56	1.07	2	HPLC	0.54	0	0	a
14	3.29	3.02	3.72	3.34	1.17	2	GC-MS/MS	0.59	-0.3	-0.4	a
15	1.38	1.55	1.58	1.5	0.2	2	HPLC	0.1	-2.8	-12	b
16						2					
17	3.36	3.46	3.28	3.37	0.56	2	GC-MS/MS	0.28	-0.3	-0.6	a
18	3.24	3.06	3.11	3.1	0.63	2	GC-MS	0.32	-0.6	-1.3	a
19	5.86	5.82	5.33	5.67	0.75	2	HPLC	0.37	2.9	5.2	a
20	3.8	3.8	3.8	3.8	0.8	2	GC_HRMS	0.4	0.3	0.6	a
21	3.7	3.7	4.2	3.9	0.5	2	HPLC	0.25	0.5	1.2	a
22	3.8	3.6	3.7	3.7	0.8	2	GC-MS	0.4	0.2	0.3	a
23	8.72	6.64	9.67	8.34	0.83	2	GC-MS	0.41	6.5	10.9	a
24	5.93	5.94	6.12	6	0.5	2	HPLC	0.25	3.3	8.5	a
25	3.39	3.45	3.3	3.39	0.57	2	GC-MS	0.29	-0.2	-0.5	a
26	2.93	2.38	3.51	2.94	0.85	2	HPLC	0.42	-0.8	-1.4	a
27	3.4	3.6	3.6	3.5	0.63	2	GC-MS/MS	0.32	-0.1	-0.2	a
28	3.07	3.14	3.74	3.32	0.34	2	GC-MS	0.17	-0.3	-1.1	a
29						2					
30	3.2	3.1	3.2	3.2	0.96	2	GC-MS/MS	0.48	-0.5	-0.7	a
31	5.29	5.04	5.18	5.17	0.83	2	GC-MS	0.42	2.2	3.7	a
32	3.77	4.25	3.79	3.94	0.59	2	GC-MS	0.29	0.5	1.2	a
33	10.55	6.24	7.03	6.64	1.33	2	GC-MS/MS	0.66	4.2	4.5	a
34	3.3	3.5	3.8	3.5	0.98	2	GC-MS/MS	0.49	-0.1	-0.1	a
35	3.6	3.6	3.7	3.6	1.2	2	GC-MS	0.6	0.1	0.1	a
36				1.61	0.48	2	GC-MS/MS	0.24	-2.7	-7	a
37	3.66	3.82	3.83	3.77	0.75	2	HPLC	0.37	0.3	0.5	a
51	3.78	3.92	4.06	3.92	1.18	2	GC-MS/MS	0.59	0.5	0.6	a
52	3.42	3.23	3.54	3.4	0.68	2	GC-MS/MS	0.34	-0.2	-0.4	a
53	3.9	3.4	3.3	3.5	1.05	2	HPLC	0.53	-0.1	-0.1	a
54	3.2	3.1	3.2	3.2	0.3	2	GC-MS/MS	0.15	-0.5	-1.7	a
55	3.66	3.71	3.61	3.66	0.73	2	GC-MS/MS	0.37	0.1	0.3	a
56	3.79	3.56	3.35	3.57	0.71	2	GC-MS/MS	0.36	0	0	a
57	3.48	4.86	3.64	4.17	0.83	2	HPLC	0.41	0.8	1.4	a
58	3.4	3.3	3.4	3.4	0.8	2	GC-MS	0.4	-0.2	-0.4	a
59	3.3	3.28	3.22	3.27	0.97	2	GC_HRMS	0.48	-0.4	-0.6	a
60	3.89	3.64	3.8	3.8	1.7	2	HPLC	0.85	0.3	0.3	c
61	3.7	3.6	3.6	3.6	1.4	1	GC-MS	1.4	0.1	0	c
62	3.65	3.36	3.14	3.38	0.71	2	HPLC	0.35	-0.2	-0.5	a
63	4.55	4.51	4.77	4.61	0.63	2	GC-MS/MS	0.32	1.4	3	a
64	3.4	3.2	3.3	3.3	0.88	2	HPLC	0.44	-0.4	-0.6	a
65	3.53	3.56	3.61	3.57	0.71	2	GC-MS/MS	0.36	0	0	a
66	3	3.61	2.88	3.16	0.25	2	GC-MS/MS	0.13	-0.5	-2.1	b
67	7.92	5.17		6.54	1.58	2	GC-MS/MS	0.79	4.1	3.7	c
68	3.67	3.83	3.79	3.67	1.17	2	GC-MS/MS	0.58	0.2	0.2	a
69	2.75	2.79		2.77	0.9	2	GC-MS	0.45	-1.1	-1.7	a
70	4.15	4.13	4.14	4.14	0.1	2	HPLC	0.05	0.8	3.8	b
71	5.1	5.12	4	4.74	0.85	2	GC-MS/MS	0.43	1.6	2.6	a
72	2.82	2.57	2.64	2.7	0.81	2	HPLC	0.41	-1.2	-2	a
73	3.58	3.44	3.62	3.58	0.47	2	GC-MS/MS	0.23	0	0.1	a

Satisfactory, Questionable, **Unsatisfactory**

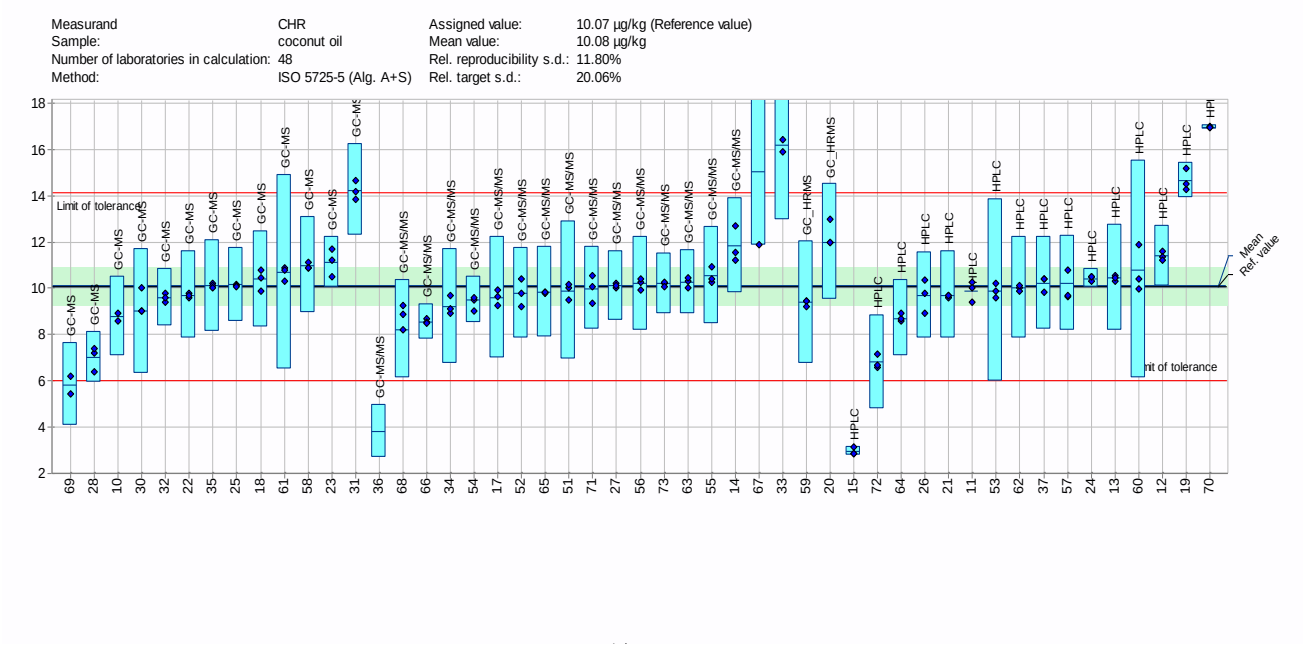
a : $u_{ref} \leq u_{lab} \leq u_{max}$ (σ_p);

b : $u_{lab} < u_{ref}$;

c : $u_{lab} > u_{max}$ (σ_p)

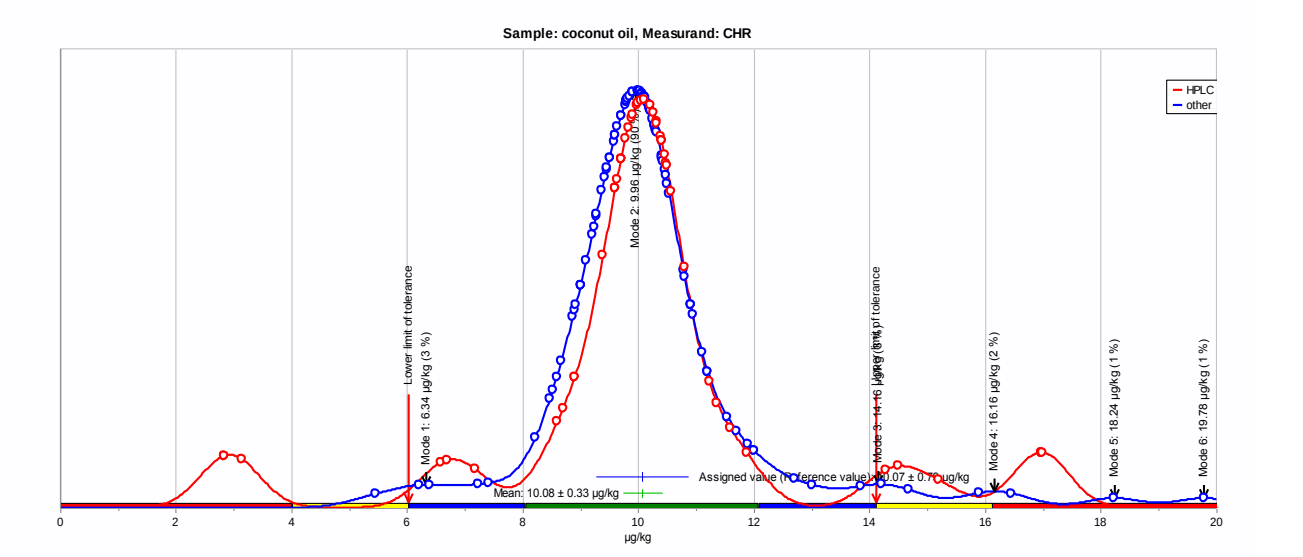
Distribution of individual results of replicate determinations reported for the <u>chrysene</u> (CHR) content of the coconut oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the chrysene (CHR) content of the coconut oil test sample

Red dots and line - HPLC results; blue dots and lines - GC-mass spectrometry results



Results, as reported by the participants, for the content of chrysene (CHR) of the coconut oil test sample.

Due to a software problem, the reported significant zeros after the comas are missing

Lab code	M 1	M 2	M 3	X lab	U lab	k	Analytical method	u lab	Z-Score	Zeta score	Classification
10	8.92	8.59		8.76	1.73	2	GC-MS	0.86	-0.6	-1.4	a
11	9.39	10.26	10.04	9.9		2	HPLC		-0.1		
12	11.59	11.36	11.22	11.39	1.3	2	HPLC	0.65	0.7	1.7	a
13	10.57	10.31	10.45	10.44	2.3	2	HPLC	1.15	0.2	0.3	a
14	12.7	11.54	11.2	11.82	2.06	2	GC-MS/MS	1.03	0.9	1.6	a
15	3.14	2.84	2.83	2.94	0.2	2	HPLC	0.1	-3.5	-17.5	b
16						2					
17	9.64	9.91	9.28	9.61	2.63	2	GC-MS/MS	1.31	-0.2	-0.3	a
18	10.78	9.9	10.45	10.4	2.08	2	GC-MS	1.04	0.2	0.3	a
19	14.28	14.5	15.19	14.66	0.75	2	HPLC	0.37	2.3	8.4	b
20	13	12	12	12	2.5	2	GC_HRMS	1.25	1	1.5	a
21	9.6	9.7	9.7	9.7	1.9	2	HPLC	0.95	-0.2	-0.4	a
22	9.8	9.6	9.7	9.7	1.9	2	GC-MS	0.95	-0.2	-0.4	a
23	10.5	11.7	11.2	11.1	1.1	2	GC-MS	0.55	0.5	1.5	a
24	10.32	10.49	10.48	10.43	0.42	2	HPLC	0.21	0.2	0.8	b
25	10.15	10.11	10.09	10.15	1.61	2	GC-MS	0.8	0	0.1	a
26	9.78	8.9	10.38	9.69	1.87	2	HPLC	0.94	-0.2	-0.4	a
27	10.2	10	10.1	10.1	1.51	2	GC-MS/MS	0.76	0	0	a
28	7.22	6.38	7.4	7	1.1	2	GC-MS	0.55	-1.5	-4.5	a
29						2					
30	9	10	9	9	2.7	2	GC-MS	1.35	-0.5	-0.8	a
31	13.85	14.2	14.67	14.24	1.99	2	GC-MS	1	2.1	3.9	a
32	9.42	9.77	9.57	9.59	1.25	2	GC-MS	0.62	-0.2	-0.6	a
33	19.79	15.9	16.45	16.18	3.23	2	GC-MS/MS	1.62	3	3.7	a
34	8.9	9.1	9.7	9.2	2.5	2	GC-MS/MS	1.25	-0.4	-0.7	a
35	10.2	10.1	10	10.1	2	2	GC-MS	1	0	0	a
36				3.8	1.14	2	GC-MS/MS	0.57	-3.1	-9	a
37	9.83	10.4	10.4	10.2	2	2	HPLC	1	0.1	0.1	a
51	10.02	9.5	10.18	9.9	2.97	2	GC-MS/MS	1.49	-0.1	-0.1	a
52	9.8	10.4	9.2	9.8	1.96	2	GC-MS/MS	0.98	-0.1	-0.3	a
53	9.9	10.2	9.6	9.9	3.96	2	HPLC	1.98	-0.1	-0.1	a
54	9.5	9	9.6	9.5	1	2	GC-MS/MS	0.5	-0.3	-0.9	a
55	10.28	10.94	10.41	10.54	2.11	2	GC-MS/MS	1.05	0.2	0.4	a
56	10.25	10.42	9.91	10.19	2.04	2	GC-MS/MS	1.02	0.1	0.1	a
57	9.63	10.79	9.7	10.21	2.04	2	HPLC	1.02	0.1	0.1	a
58	11.1	10.9	10.9	11	2.1	2	GC-MS	1.05	0.5	0.8	a
59	9.46	9.45	9.23	9.38	2.66	2	GC_HRMS	1.33	-0.3	-0.5	a
60	11.88	9.97	10.4	10.8	4.7	2	HPLC	2.35	0.4	0.3	c
61	10.9	10.8	10.3	10.7	4.2	1	GC-MS	4.2	0.3	0.1	c
62	10	9.88	10.1	10	2.2	2	HPLC	1.1	0	-0.1	a
63	10.01	10.31	10.47	10.26	1.4	2	GC-MS/MS	0.7	0.1	0.2	a
64	8.6	8.7	8.9	8.7	1.66	2	HPLC	0.83	-0.7	-1.5	a
65	9.84	9.79	9.82	9.82	1.96	2	GC-MS/MS	0.98	-0.1	-0.2	a
66	8.67	8.52	8.47	8.55	0.77	2	GC-MS/MS	0.38	-0.8	-2.8	b
67	18.23	11.89		15.06	3.2	2	GC-MS/MS	1.6	2.5	3	a
68	8.22	9.27	8.87	8.22	2.14	2	GC-MS/MS	1.07	-0.9	-1.6	a
69	6.2	5.45		5.83	1.8	2	GC-MS	0.9	-2.1	-4.3	a
70	16.98	16.96	16.97	16.97	0.1	2	HPLC	0.05	3.4	17.3	b
71	10.53	10.06	9.37	9.98	1.8	2	GC-MS/MS	0.9	0	-0.1	a
72	7.17	6.58	6.69	6.8	2.04	2	HPLC	1.02	-1.6	-3	a
73	10.19	10.28	10.07	10.19	1.32	2	GC-MS/MS	0.66	0.1	0.2	a

Satisfactory, Questionable, **Unsatisfactory**

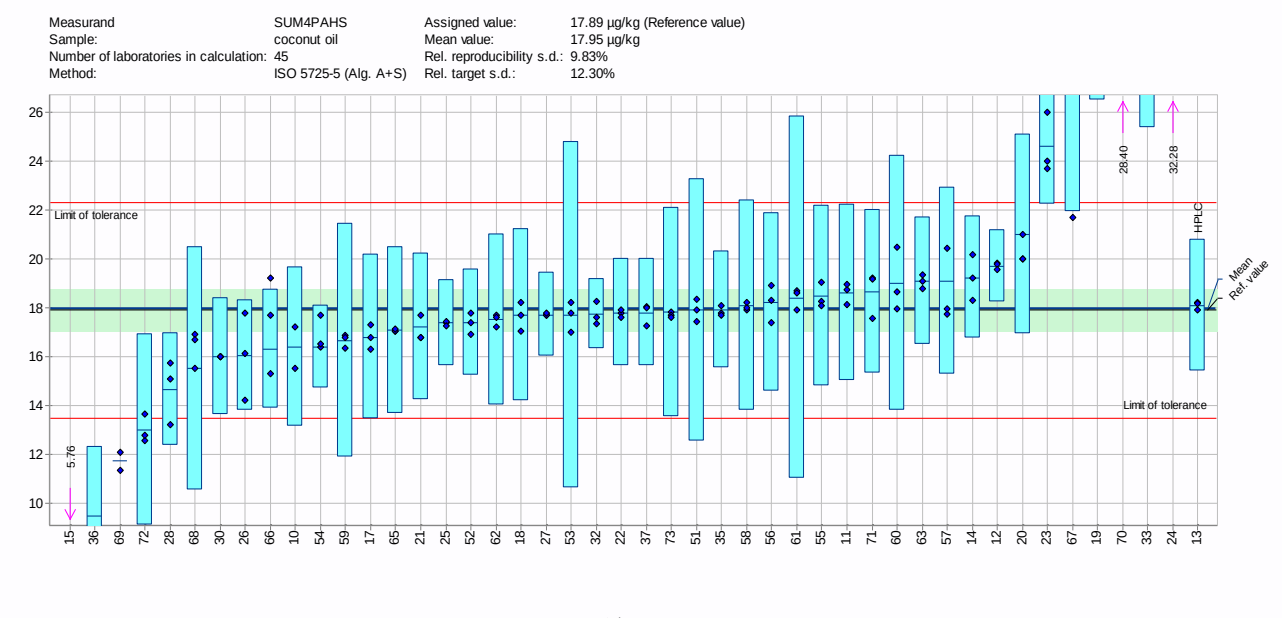
a : $u_{ref} \leq u_{lab} \leq u_{max}$ (σ_p);

b : $u_{lab} < u_{ref}$;

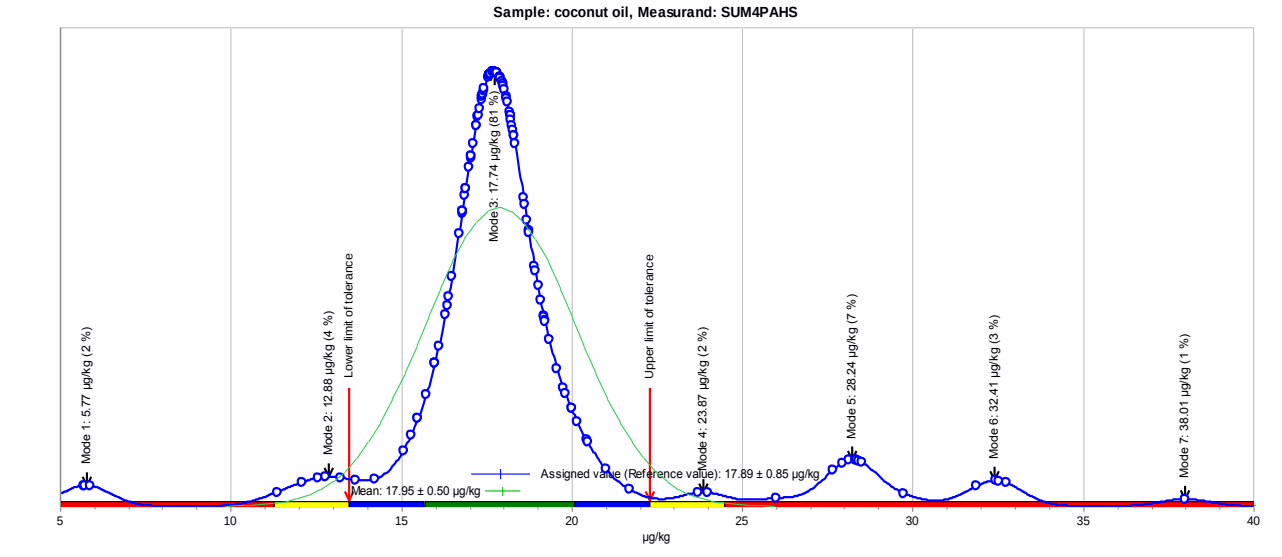
c : $u_{lab} > u_{max}$ (σ_p)

Distribution of individual results of replicate determinations reported for the <u>sum of the four markers PAHs</u> (SUM4PAH) content of the coconut oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, green area around assigned value: expanded uncertainty of the assigned value (k=2), red lines: lower and upper limit of satisfactory z-score range;



Kernel density plot of the reported values for proficiency assessment for the SUM4PAH content of the coconut oil test sample



Results, as reported by the participants, for the sum of the four markers PAHs (SUM4PAH) of the coconut oil test sample.

Due to a software problem, the reported significant zeros after the comas are missing

Lab code	M 1	M 2	M 3	X lab	U lab	k	u lab	Z-Score	Zeta score	Classification
10	17.2	15.5		16.4	3.25	2	1.62	-0.7	-0.9	a
11	18.75	18.94	18.12	18.6	3.61	2	1.8	0.3	0.4	a
12	19.82	19.76	19.58	19.71	1.48	2	0.74	0.8	2.1	a
13	18.23	17.91	18.18	18.1	2.69	2	1.35	0.1	0.1	a
14	20.17	18.31	19.22	19.23	2.51	2	1.25	0.6	1	a
15	5.88	5.68	5.71	5.76	0.2	2	0.1	-5.5	-27.8	b
16						2				
17	16.8	17.3	16.3	16.8	3.38	2	1.69	-0.5	-0.6	a
18	18.2	17.05	17.7	17.7	3.53	2	1.77	-0.1	-0.1	a
19	28.34	27.66	27.94	27.98	1.5	2	0.75	4.6	11.7	a
20	21	20	20	21	4.1	2	2.05	1.4	1.5	a
21	16.8	16.8	17.7	17.2	3	2	1.5	-0.3	-0.4	a
22	17.8	17.9	17.6	17.8	2.2	2	1.1	0	-0.1	a
23	24	23.7	26	24.6	2.4	2	1.2	3	5.3	a
24	31.88	32.43	32.54	32.28	3.2	2	1.6	6.5	8.7	a
25	17.38	17.44	17.26	17.38	1.76	2	0.88	-0.2	-0.5	a
26	16.11	14.23	17.8	16.05	2.25	2	1.13	-0.8	-1.5	a
27	17.7	17.7	17.8	17.7	1.72	2	0.86	-0.1	-0.2	a
28	15.07	13.21	15.74	14.67	2.3	2	1.15	-1.5	-2.6	a
29						2				
30	16	16	16	16	2.4	2	1.2	-0.9	-1.5	a
31				25.82	7.51	2	3.76	3.6	2.1	c
32	17.36	18.26	17.59	17.74	1.43	2	0.71	-0.1	-0.2	a
33	38	28.13	29.75	28.94	3.6	2	1.8	5	6	a
34				17	2.8	2	1.4	-0.4	-0.6	a
35	18.1	17.8	17.7	17.9	2.4	2	1.2	0	0	a
36				9.48	2.84	2	1.42	-3.8	-5.7	a
37	17.25	18.03	17.98	17.8	2.2	2	1.1	0	-0.1	a
51	17.9	17.42	18.35	17.89	5.37	2	2.68	0	0	c
52	17.4	17.8	16.9	17.4	2.17	2	1.09	-0.2	-0.4	a
53	18.2	17.8	17	17.7	7.08	2	3.54	-0.1	-0.1	c
54	16.4	17.7	16.5	16.4	1.7	2	0.85	-0.7	-1.6	a
55	18.28	19.02	18.08	18.46	3.69	2	1.85	0.3	0.3	a
56	18.92	18.31	17.39	18.21	3.64	2	1.82	0.1	0.2	a
57	17.74	20.44	17.95	19.09	3.82	2	1.91	0.5	0.6	a
58	18.2	17.9	18	18.1	4.3	2	2.15	0.1	0.1	a
59	16.87	16.79	16.35	16.66	4.79	2	2.4	-0.6	-0.5	c
60	20.48	17.95	18.63	19	5.2	2	2.6	0.5	0.4	c
61	18.7	18.6	17.9	18.4	7.4	1	7.4	0.2	0.1	c
62	17.7	17.2	17.6	17.5	3.5	2	1.75	-0.2	-0.2	a
63	18.76	19.1	19.35	19.07	2.61	2	1.31	0.5	0.9	a
64						2				
65	17.04	17.05	17.11	17.07	3.41	2	1.71	-0.4	-0.5	a
66	17.7	19.23	15.3	16.3	2.44	2	1.22	-0.7	-1.2	a
67	32.74	21.71		27.23	5.3	2	2.65	4.2	3.5	c
68	15.5	16.9	16.7	15.5	4.96	2	2.48	-1.1	-0.9	c
69	12.1	11.36		11.73	0	2	0	-2.8		b
70	28.43	28.51	28.32	28.4	0.1	2	0.05	4.8	24.6	b
71	19.2	19.19	17.57	18.65	3.36	2	1.68	0.3	0.4	a
72	13.66	12.56	12.77	13	3.9	2	1.95	-2.2	-2.5	a
73	17.82	17.69	17.62	17.82	4.28	2	2.14	0	0	a

Satisfactory, **Questionable**, **Unsatisfactory**

a : $u_{ref} \leq u_{lab} \leq u_{max}\ (\sigma_p)$;

b : $u_{lab} < u_{ref}$;

c : $u_{lab} > u_{max}\ (\sigma_p)$

Europe Direct is a service to help you find answers to your questions about the European Union
Free phone number (*): 00 800 6 7 8 9 10 11
(*) Certain mobile telephone operators do not allow access to 00 800 numbers or these calls may be billed.

A great deal of additional information on the European Union is available on the Internet.
It can be accessed through the Europa server http://europa.eu

How to obtain EU publications

Our publications are available from EU Bookshop (http://bookshop.europa.eu),
where you can place an order with the sales agent of your choice.

The Publications Office has a worldwide network of sales agents.
You can obtain their contact details by sending a fax to (352) 29 29-42758.

KJ-NA-28741-EN-N

JRC Mission

As the science and knowledge service of the European Commission, the Joint Research Centre's mission is to support EU policies with independent evidence throughout the whole policy cycle.

EU Science Hub
ec.europa.eu/jrc

@EU_ScienceHub
EU Science Hub - Joint Research Centre
Joint Research Centre
EU Science Hub

Publications Office

doi:10.2760/816638

ISBN 978-92-79-72236-3